VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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INFLUENCE OF CARBON NANOTUBES ON THE EFFECTIVENESS OF PLASTICIZERS, HYDRATION AND STRUCTURE OF CEMENT-BASED MATERIALS

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VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

Ekaterina KARPOVA

ANGLIES NANOVAMZDELIŲ POVEIKIS PLASTIFIKUOJANČIŲ ĮMAIŠŲ EFEKTYVUMUI, CEMENTINIŲ MIŠINIŲ HIDRATACIJAI IR STRUKTŪRAI

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Abstract

This work aims to investigate the effect of multi-walled carbon nanotubes (MWCNT) suspension in combination with plasticizing admixtures (Pl) on the rheological and technological properties of cement-based materials. The study of the cement hydration process, structure and properties of modified cement-based materials were performed.

The different types of Pl, such as lignosulphonate (LS), sulfonated naphthalene formaldehyde condensate (NF) and polycarboxylate ether (PCE) were used in the course of the research. The homogenization of MWCNT in the aqueous suspension was provided by the ultrasonication method. It was established that the usage of PCE contributes to the increase of the average diameter of the particles caused by the intermolecular interactions between the carboxyl groups of the carboxymethyl cellulose (CMC) located on the MWCNT surface and the carboxylate groups of PCE with further formation of the hydrogen bonds.

The rheological properties of cement paste modified by MWCNT suspension with different Pl were tested by the rotational rheometer with coaxial cylinders at 5, 60, 120 min after cement paste mixing. The yield stress, plastic viscosity and shear thinning/ shear thickening indexes were evaluated for the tested cement pastes based on the experimental data and their approximation by the Hershel-Bulkley rheological model. The increase of MWCNT dosages from 0 to 0.24% bwoc provided the changes in rheological properties of cement pastes. The essential reduction of water bleeding and high stability of cement paste were achieved with MWCNT modification.

In addition to the rheological tests, the calorimetry, setting time, structure formation investigation of the cement-based materials with MWCNT and different Pl were undertaken. The addition of MWCNT caused the acceleration of the Portland cement hydration, increase in total emitted heat and changes in the morphology of the cement hydration products.

The dissertation is composed of an introduction, three chapters (literature survey, experimental methodology, and discussion of the results), general conclusions, lists of references, sources, and author's publications on the subject of the dissertation, summary in Lithuanian and seven annexes.

The author has published 12 articles on the topic of the dissertation (two of them in the journals with the citation index referred by the Clarivate Analytics Web of Science).

Reziumė

Šio darbo tikslas – ištirti daugiasluoksnių anglies nanovamzdelių (MWCNT) suspensijos kartu su plastifikuojančiomis įmaišomis (Pl) poveikį mišinių su cementiniais rišikliais reologinėms ir technologinėms savybėms. Taip pat ištirtas tokių mišinių hidratacijos procesas, mikrostruktūra ir savybės.

Tyrimo metu buvo naudojami skirtingi Pl tipai, tokie kaip lignosulfonatas (LS), sulfonintas naftaleno formaldehidas (NF) ir polikarboksilato eteris (PCE). MWCNT homogenizavimui vandeninėje suspensijoje buvo panaudotas ultragarsinis metodas. Nustatyta, kad PCE įvedimas padidina vidutinį dalelių skersmenį suspensijoje dėl tarpmolekulinės sąveikos tarp karboksimetilceliuliozės (CMC) karboksilo grupių, esančių ant MWCNT paviršiaus, ir PCE karboksilato grupių, dėl ko formuojasi vandenilinės jungtys.

Cemento tešlų, modifikuotų MWCNT suspensija su skirtingais Pl, reologinės savybės išbandytos rotaciniu reometru su koaksialiniais cilindrais 5, 60, 120 min po cemento tešlos sumaišymo. Pagal gautus eksperimentinius rezultatus buvo nustatyti cemento tešlų šlyties įtempiai, plastinis klampis ir tiksotropiškumo/ dilatantiškumo rodikliai naudojant Hershel-Bulkley reologinį modelį. MWCNT kiekio padidinimas nuo 0 iki 0,24% cemento masės sukelia cementinių tešlų reologinių savybių pokyčius. Modifikuojant cemento tešlą MWCNT suspensija buvo pasiektas žynus vandens atsiskyrimo sumažėjimas ir didelis cemento tešlos stabilumas.

Be reologinių bandymų, buvo atliktas cementinių mišinių, modifikuotų MWCNT ir skirtingais Pl, kalorimetrijos, rišimosi terminų, struktūros formavimosi tyrimai. MWCNT priedas pagreitina portlandcemenčio hidrataciją, padidina hidratacinės šilumos kiekį ir pakeičia cemento hidratacijos produktų morfologiją.

Disertaciją sudaro įvadas, trys skyriai (literatūros apžvalga, eksperimentinė metodika ir rezultatų aptarimas), bendrosios išvados, literatūros šaltinių sąrašas, autoriaus paskelbtų disertacijos tema publikacijų sąrašas, santrauka lietuvių kalba ir septyni priedai.

Autorė paskelbė 12 straipsnių disertacijos tema (du iš jų, žurnaluose su citavimo indeksu Clarivate Analytics Web of Science duomenų bazių žurnaluose).

Notations

Symbols

$\dot{\gamma}$ – shear rate, s^{-1};

σ – surface tension, mN/m;

τ – shear stress, Pa;

τ_0 – yield stress of the cement paste, Pa;

a – initial volume of cement paste, cm^3 (in the bleeding test);

b – volume of sedimented cement, cm^3 (in the bleeding test);

d – density of a liquid, g/cm^3 (in the surface tension measurements);

μ – plastic viscosity, Pa·s;

K_b – coefficient of water bleeding, %;

n – shear thinning or shear thickening index if $n < 1$ or $n > 1$, respectively;

N – number of drops (in surface tension measurements);

W/C – water to cement ratio.

Abbreviations

AS – amino sulfonate;
BET – Brunauer-Emmett-Teller (equation);
bwoc – by weight of cement;
CMC – carboxymethyl cellulose;
CNT – carbon nanotubes;
FTIR – Fourier-transform infrared (spectroscopy);
GNP – nano graphite platelets;
GO – graphene oxide;

HWC – high workability concrete;
LS – lignosulfonate;
MS – melamine sulfonate;
MWCNT – multi-walled carbon nanotubes;
NF – sulfonated naphthalene formaldehyde condensate;
PCA – polycarboxylate acid;
PCE – polycarboxylate ether;
PDI – polydispersity index;
Pl – plasticizer, plasticizing admixture;
SCC – self-compacting concrete;
SEM – scanning electron microscopy;
SP – superplasticizer;
STA – simultaneous thermal analysis;
UZ – ultrasonication;
XRD – X-ray diffraction (analysis).

Definitions

Water bleeding – the emergence of free water on the surface of newly placed concrete.

Carbon nanotubes – the cylinders consisting of rolled-up graphite planes with diameters of nanometer-scale and a length-to-diameter ratio higher than 1000000. Carbon nanotubes can be single- and multi-walled depends on amounts of graphene layers.

Cement-based material (Cement composite) – mixture with Portland cement binding material (with or without additives), and with or without different aggregates (micro filler, sand or coarse aggregates), such as cement paste, mortar or concrete in a fresh and hardened state.

Dilatancy (shear thickening behaviour) – the behaviour of cement paste which is characterized by the increase of apparent viscosity when shear rate increases.

Effectiveness of plasticizers – the indicator of the effect of plasticizing admixture in the same dosage on the changes in yield stress, plastic viscosity and rheological behaviour of cement paste and maintaining these parameters during the time after cement paste mixing.

Homogenization – the process of the equal distribution of CNT in the volume of an aqueous suspension.

Nanoparticles – particles with one of the structural dimension up to 100 nm with high specific surface area and surface energy.

Plasticizer (plasticizing admixture) – admixture for concrete which decreases the water content of concrete mixture without changes in consistency or which increases slump/flow of concrete mixture without changes in water content. The plasticizing admixture with water reduction capability more than 5% and less than 12% can be classified as a plasticizer, and with water reduction capability more than 12% can be classified as a superplasticizer.

Plastic viscosity – a resistance of cement paste to flow which can be expressed as the coefficient of proportionality between an increment in shear stress and the corresponding increment in shear rate.

Polydispersity index – a system homogeneity parameter that changes from 0 to 1.

Surface tension – the tendency of a liquid to reduce excess potential energy at the interface with another medium.

Suspension – heterogeneous mixture with solid dispersion phase and liquid dispersion medium.

Thixotropy (shear thinning behaviour) – the behaviour of cement paste which is characterized by the decrease of apparent viscosity when shear rate increases.

Yield stress – the minimum shear stress which can cause the flow of cement paste.

Zeta potential – an electrokinetic potential which develops at the boundary between the compact layer and the diffuse layer and used as a parameter of the suspension stability.

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Introduction

Problem Formulation

The development of pumping technology and the design of self-compacting concrete (SCC) are one of the crucial topics in modern concrete technology. The wide range of plasticizing admixtures (Pl) contributes to the improvement of the rheological and technological properties of concrete in different ways, but, as it is mentioned in the number of modern researches, there are not fully understanding in their action mechanisms and exact rheological models. The production of high workability concrete requires providing not only high workability, but also stability of concrete to the water bleeding and the segregation. In this case, the generation of new complex admixtures is becoming necessary.

With the development of nanotechnology, the interest in the application of carbon nanotubes (CNT including MWCNT) for concrete modification is increasing from year to year. The CNT can be used as a component of complex admixtures due to their outstanding properties. The main issue in the application of CNT is linked with their ability to coagulation caused by huge specific surface area and strong Van der Waals forces between them. The searching for the rational homogenization methods of CNT, optimal methods of suspension control, comprehension of hydration, rheology of fresh cement pastes and a formation of hardened cement paste with CNT require further investigation.

Relevance of the Thesis

The application of Pl for the improvement of the rheological and technological properties, cement hydration process and microstructure of hardened cement paste is becoming more widely used in concrete technology. The CNT due to unique fineness, physical and mechanical properties in combined application with Pl can have an effect on the plasticizing efficiency, rheological behaviour and stability of mixtures, and, as a consequence, improve the properties of cement-based materials in a fresh state and hardened state after cement hydration process. Despite the significant number of researches, the mechanisms of combined interactions of CNT and different types of Pl in the cement-based mixture are not completely clarified and require further investigation.

Object of the Research

The object of research is the cement-based materials modified by MWCNT suspension with plasticizing admixtures in a fresh and hardened state.

Aim of the Thesis

The research aim is to identify the interaction mechanism between MWCNT and plasticizing admixtures by determining its effect on rheological properties of cement-based mixtures, hydration process of cement, and microstructure of hardened cement paste.

Tasks of the Thesis

In order to achieve the aim of the thesis, the following tasks are formulated:

1. To establish the methodology of the suspension homogenization according to the content of MWCNT and type of plasticizing admixture, the optimal type and intensity of suspension homogenization method. To evaluate the properties of MWCNT suspension after homogenization and establish the behaviour of the MWCNT suspension during the ageing.
2. To evaluate the rheological properties of cement pastes modified by MWCNT suspension in combination with different types of plasticizing admixtures and without them. To identify the dosages of MWCNT

suspension which have an impact on yield stress, plastic viscosity and shear thinning (thickening) indexes.

3. To investigate the influence of MWCNT suspension on the stability of cement pastes with different plasticizing admixtures and without them.
4. To investigate the effect of MWCNT suspension on the hydration kinetics of cement paste, mineral composition and microstructure of hardened cement paste in combination with different plasticizing admixtures and without them.

Research Methodology

The present study involves the methodology of MWCNT suspension homogenization and characterization, the methodology of the rheological test of modified cement paste and the methodology of modified cement composites microstructure testing.

The homogenization of MWCNT suspension was performed by the probe type ultrasonication. The characterization of prepared MWCNT suspension was carried out via pH, electrical conductivity, zeta potential, surface tension, particle size analysis and FTIR spectroscopy.

The rheological test was provided by the rotational rheometer with coaxial cylinders at different time after cement paste mixing using specially selected shear rate mode during the time. The experimental rheological data were processed according to the Herschel-Bulkley model.

Hydration process of cement pastes was tested by the isothermal calorimeter. The microstructure and morphology were investigated by the methods of XRD, thermal analysis, nitrogen adsorption-desorption porosimetry, SEM and FTIR spectroscopy.

Scientific Novelty of the Thesis

The thesis preparation led to the new materials engineering science results:

1. The complex action mechanism of MWCNT and plasticizing admixtures of different genesis in cement-based materials was identified.
2. MWCNT dosages affecting the rheological parameters (yield stress, plastic viscosity, shear thinning/ thickening indexes) and resistance to water bleeding of plasticized and not plasticized cement pastes were obtained.

3. The parameters of the cement hydration process for cement-based materials modified by MWCNT suspension in combination with different types of plasticizing admixtures were established.

Practical Value of the Research Findings

The results of the investigation can be used for the development of complex admixtures with MWCNT and plasticizing admixture for cement-based materials (mortars, concretes and others). The managing by the flow behaviour and hydration process of cement-based materials through modification by complex admixture may be applied for the improvement of concrete transportation, handling, pumping and compacting technologies. Moreover, the complex admixtures with MWCNT can provide the production of concrete mixtures without water bleeding for different technical application, such as concrete with high-workability, self-compacting performance and concrete mixtures for 3D printing technology.

The Defended Statements

1. Due to high fineness and surface area of particles, MWCNT in combination with various plasticizing admixtures change the plasticizing effect of admixtures and decrease water bleeding of cement-based materials.
2. The addition of MWCNT accelerates the hydration processes of plasticized cement-based materials due to physical interactions such as intermolecular, electrokinetic and others.
3. MWCNT do not lead to the formation of new phases of the cement hydration products due to the absence of chemical reactivity. MWCNT change the morphology of the cement matrix through its physical interactions with cement hydration products.

Approval of the Results

The author has published 12 articles on the topic of the dissertation: two in scientific journals, included into publications of the *Clarivate Analytics Web of Science* database, with an impact factor (Skripkiunas *et al.*, 2018; Skripkiunas *et al.,* 2019) and one article without an impact factor (Skripkiunas *et al.* 2019), four articles in publications of other databases (Karpova *et al.*, 2014; Karpova *et al.*, 2015; Skripkiunas *et al.*, 2017; Karpova *et al.*, 2019), three arti-

cles in conference proceedings referred by the *Clarivate Analytics Web of Science* (Yakovlev *et al.*, 2019; Skripkiunas *et al.*, 2019a; Skripkiunas *et al.*, 2019b), two articles in conference proceedings of other databases (Skripkiunas *et al.*, 2018a; Skripkiunas *et al.*, 2018b). During the PhD study period (2016–2020) the author has made 12 presentations at 12 scientific conferences:

- 2019. The 4th International Conference on *Innovative Materials, Structures and Technologies.* Riga, Latvia.
- 2019. The 13th International Conference on *Modern Building Materials, Structures and Techniques.* Vilnius, Lithuania.
- 2018. The 5th International Conference on *Nanotechnologies.* Tbilisi, Georgia.
- 2018. The 6th International Scientific Conference on *Integration, Partnership and Innovation in Construction Science and Education.* Moscow, Russian Federation.
- 2018. The 14th Cross-Strait Workshop on *Nano Science and Technology.* Macau, China (absentee participation).
- 2018. The 3rd *World Multidisciplinary Civil Engineering, Architecture, Urban Planning Symposium*. Prague, Czech Republic.
- 2017, 2019. The 5th, 7th International Conference on *Binders and Materials.* Brno, Czech Republic.
- 2017, 2018. The 20th, 21th Conference for Junior Researchers *Science – Future of Lithuania.* Vilnius, Lithuania.
- 2017. The 19th International *Conference of PhD Students*. Brno, Czech Republic.
- 2016. The International Scientific-Technical Conference on *High-strength Cement Concretes: Technologies, Constructions, and Economics.* Kazan, Russia.

Structure of the Dissertation

The dissertation consists of an introduction, three chapters, general conclusions, literature reference list (159 publications), list of the author's publications on the research topic (12 publications), summary in Lithuanian and 7 annexes. The volume of the dissertation is 142 pages. The text contains 3 equations, 13 tables, and 73 figures.

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1

Effect of Plasticizers and Nanotubes on the Properties of Cement-Based Materials

This chapter reviews the effect of widely used plasticizing admixtures (Pl) on the properties of cement pastes in a fresh and hardened state. The methods of homogenization of MWCNT suspension and its influence on the properties of cement-based materials are considered as well. This chapter also formulates the main objective and tasks of the present investigation. This chapter includes the material presented in journal publication Skripkiunas *et al.* (2017), Skripkiunas *et al.* (2018), Skripkiunas *et al.* (2019), Karpova *et al.* (2019) and conference proceedings Skripkiunas *et al.* (2018a), Skripkiunas *et al.* (2018b).

1.1. The Plasticizing Effect of Admixtures in the Cement-Based Materials

The transport, pouring, pumping, compaction and casting of modern concrete require the introduction of Pl. Pl allow improving the workability of the concrete mixture without changing of the water to cement (W/C) ratio and, as a consequence, manage by the properties of concrete in the hardened state, such as strength and durability. Moreover, the application of Pl can promote the reduction of negative impact on the environment due to the decrease of cement content used for concrete production.

Pl consists of long-chain organic molecules with hydrophilic and hydrophobic radicals, which provide the adsorption of Pl on the cement-water interface. Lignosulfonic acid, hydroxylated carboxylic, polysaccharides and their derivatives are the basis of Pl which are used nowadays for cement-based materials plasticizing. The orientation of polar radicals of Pl to the water enables to decrease the surface tension of water and provide the hydrophilicity of cement particles. As a consequence of Pl action, the flocculation is prevented, and well distribution of cement particles is achieved (Kumar & Monteiro 2006).

The application of Pl is back to the 1930s when production of natural mid-range water reducers was started. Lignosulphonate (LS) is one of the natural polymer Pl which is obtained as by-products of bisulphite pulping of wood. LS is still widely used in concrete technology in view its low price in comparison with other types of synthetic plasticizing admixtures. However, LS posses the limited water-reduction ability of about 10% with an average applied dosage of about 0.1–0.3% by weigh of cement (bwoc) and does not increase the compressive strength of cement composites significantly (Aitcin & Flatt 2016a). LS contains numerous functional groups, such as carboxylic acid, phenolic hydroxyl, cathechol, methoxyl, sulfonic acid and various combinations of them. LS molecules form the spherical microgels or sheet-like structures with a generation of polyelectrolyte complexes with cations, such as Ca^{2+} and Al^{3+} in cement suspensions (Houst *et al.* 2008).

The dispersing effect of LS consists of electrostatic repulsion between the cement particles when negatively charged functional groups of LS adsorb on the cement particles. This adsorption leads to the development of double electrical layer on the surface of cement particles, the occurrence of electrokinetic potential (zeta potential) on the cement particles surfaces and a consequent appearance of the electrostatic repulsion between particles (Kalliola *et al.* 2015).

The different types of LS modification are used to improve its water-reduction capability, especially, with growing interest to high workability (HWC) and self-compacting concrete (SCC) (Ouyang *et al.* 2006, Gupta *et al.* 2015, Areskogh *et al.* 2010). Ouyang *et al.* (2006) investigated the prop-

erties of cement paste with LS of different molecular weight. They established that LS with a molecular weight of 10.000–30.000 in the dosage less than 0.5 wt% leads to the maximum fluidity in cement paste. The LS modified by additional sulfonic groups with a molecular weight of 10.000 demonstrated the lower surface tension, stronger wetting and adsorption capability, higher zeta potential and, as a consequence, higher flowability in comparison with mixtures not modified by LS. Gupta *et al.* (2015) synthesized the polyacrylamide-grafted lignin via reversible addition-fragmentation chain transfer polymerization. The test of cement paste modified by synthesized LS revealed the decrease of the yield stress to similar levels as a polycarboxylate ether plasticizer (PCE), however, the dynamic viscosity was not improved. Kalliola *et al.* (2015) used alkali-O_2 oxidation method to control polymerization and solubilization of soda lignin. The oxidized lignin solutions used as Pl for concrete demonstrated superior performance and provided equal plasticizing efficiency in comparison with the synthetic LS. Areskogh *et al.* (2010) highlighted that the plasticizing ability of LS is intimately linked with the purity of LS, its molecular weight and number of charged groups in the macromolecule. The researchers modified commercial LS by laccase oxidation followed by ozonolysis to increase the molecular weight and provide the improvement of plasticizing efficiency of commercial LS.

Sulphonated naphthalene formaldehyde condensates or polynaphthalene sulphonates (NF) possesses higher water reduction capability up to 30%. NF was used as SP for concrete since the 1960s in Japan. The synthesis of NF consists of two steps, such as sulphonation of naphthalene with sulphuric acid and polycondensation in the presence of formaldehyde (Aitcin & Flatt 2016a).

The molecular structure of NF is the critical factor which influences on its dispersing ability in cement-based materials (Aitcin & Flatt 2016a). The action mechanism of NF based on electrostatic and steric repulsive forces with more pronounced electrostatic effects (Huynh *et al.* 2006, Uchikawa *et al.* 1997). NF decreases the zeta potential of cement pastes more effective than LS, which can explain to some extent its better dispersing ability in cement-based materials (Srinivasan *et al.* 2010).

However, PCE plasticizers are more efficient than NF. Yahia & Tanimure (2015) observed that mixture with belite cement and NF has relatively higher yield stress than it was for PCE. Qian & G. De Schutter (2018a) established the decrease of the yield stress of the cement paste to 0 at 0.6% bwoc of NF and the same reduction in yield stress at 0.3% bwoc of PCE. Authors concluded that PCE is more efficient in decreasing dynamic yield stress and increasing flowability in comparison with NF caused by the differences in adsorption behaviour of plasticizers, such as monolayer adsorption for NF and multi-layer adsorption for PCE.

PCE plasticizers belong to comb-shaped copolymers which are the last generation of Pl discovered in the mid-1980s. PCE possess by high water reduction capability and enable to decrease the amount of water in cement-based materials up to 40%. The comb-shaped copolymers consist of backbone presented by carboxylic groups and non-ionic polyether side chains, which are attached to the backbone (Aitcin & Flatt 2016a).

Electrostatic and steric hindrance effects underlie the action mechanism of PCE. The negatively charged backbone provides the adsorption of Pl onto the positively charged cement particles. Non-adsorbing side chains provide a steric hindrance effect. The combination of electrostatic and steric hindrance effect makes the action mechanism of PCE more efficient in comparison with other Pl. The PCE can be produced by the two ways such as free radical copolymerization and polymer analogous esterification. The chemical nature of the backbone, length and chemical nature of the side chains, distribution of the side chains along the backbone, anionic charge density and binding between backbone and side-chain play an essential role in the performance of PCE (Aitcin & Flatt 2016a).

The number of researches is devoted to the investigation of the correlation between the molecular structure of PCE and fluidity of cement pastes and concrete mixtures. Marchon *et al.* (2019) found the relationship between the dosage of a PCE, its molecular structure and given flowability. Yamada *et al.* (2000) established that PCE with longer polyoxyethylene side chain, lower degrees of backbone polymerization and higher contents of sulfonic groups possesses the higher dispersing capability of cement particles. Winnefeld *et al.* (2007) observed that PCE with higher molecular weight, lower side-chain densities and shorter side chains have stronger adsorption on the cement particles. The researchers highlighted that usage of the PCE with a low density of side chains promotes workability of cement-based materials. Dalas *et al.* (2015a) studied polymers with various side-chain lengths, grafting ratio and modified anionic functions. Researchers paid attention to the mass of adsorbed polymer and attempted to find the correlation between this mass and fluidity in cement-based materials. Moreover, they obtained that modification of anionic function groups such as carboxylate, dicarboxylate or phosphate did not improve the fluidizing efficiency of plasticizer. Liu *et al.* (2017a) designed and synthesized the PCE with star-shaped topological molecular structure, compare it with PCE of comb-shaped structure and established that the star-shaped PCE presents the better fluidity and water reduction capability. Qian *et al.* (2018b) synthesized the PCE with lowering molecular weight, side-chain length and with additional hydrophobic groups which demonstrated the improvement of dispersion capacity and viscosity-reduction efficiency. Besides the molecular structure and adsorption properties of Pl, the critical micelle concentration determines the effectiveness

of PCE in cement-based materials as well. The addition of PCE higher than critical micelle concentration provides low yield stress and high flowability (Qian *et al.* 2018c).

The balance between attractive, repulsive interparticle forces and shear forces allows influencing on the yield stress and, as a consequence, the fluidity of cement suspensions. The repulsive forces should dominate in the cement-based material to provide dispersion stability. The addition of Pl to cement suspension reduces the attractive forces between cement particles by increasing repulsive interparticle forces. Dispersion (or van der Waals), electrostatic and steric forces exist between cement particles in cement suspension. DLVO theory was developed to explain the stability of dispersions in terms of a balance between attractive (van der Waals) force and repulsive electrostatic force.

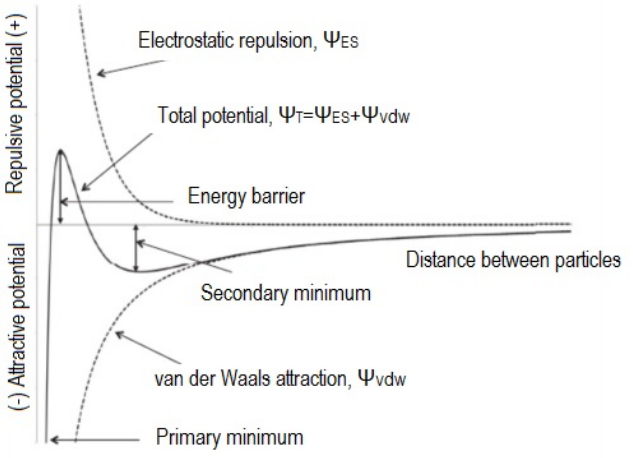


Fig. 1.1. Interparticle potentials as a function of the distance between particles (Aitcin & Flatt 2016a)

The addition of Pl increases the electrostatic repulsive forces by adsorption of admixture on the surface of cement particles and generate the steric repulsive force, which is appeared by the overlapping of the adsorption layers of admixture. The interaction forces are depending on the distance between cement particles as well. The graph in Fig. 1.1 presents the interparticle potentials as a function of the distance between particles (Aitcin & Flatt 2016a). The total interparticle force (F) in cement-based materials modified by the plasticizing admixtures can be calculated by taking the sum of dispersion (F_A), electrostatic (F_{RE}) and steric forces (F_{RS}).

Speaking about the interparticle forces between cement particles and Pl, it should be mentioned the double-layer model of Gouy-Chapman, which describe the distribution of ions in a charged interface of cement suspension. This model is presented by inner Stern layer, which consists of counter-ions and outer or diffuse layer with mobile ions. The scheme of this model is shown in Fig. 1.2 (Aitcin & Flatt 2016a).

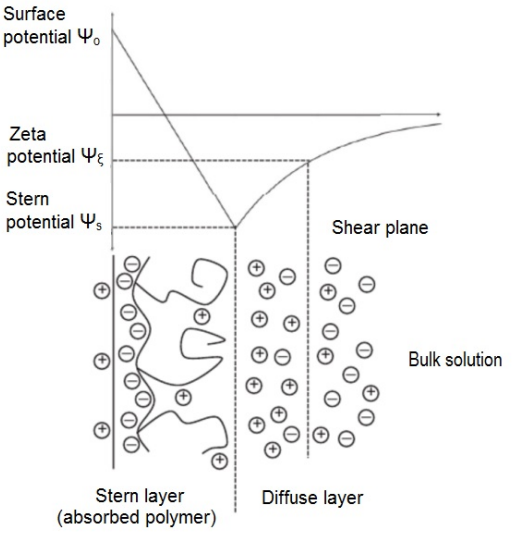


Fig.1.2. Schematic representation of the double-layer model of Gouy-Chapman (Aitcin & Flatt 2016a)

The plasticizing effect of Pl is determined by the number of factors such as changes of zeta potential, different colloidal and chemical processes on the phase boundary, adsorption processes on the surface of cement particles, properties of used cement and Pl. Cement suspension stability with Pl can be controlled by the balance of attractive and repulsive forces. The variation of molecular structures of Pl allows managing by the properties of concrete in a fresh and hardened state.

1.2. The Technological Properties and Hydration of the Cement Mixtures Modified by Plasticizing Admixtures

The various types of Pl have a different effect on the technological properties, hydration and further durability of cement-based materials. From the technological point of view, the changes in flowability and slump loss during the time of concrete mixture with Pl should be taken into consideration.

Chandra & Bjornstrom (2002) studied the effect of LS, melamine formaldehyde sulfonic acid (SMF), naphthalene formaldehyde sulfonic acid (SNF), and polyacrylic acid polymer (CE) on the flowability and slump loss of concrete. They concluded that flowability, which is mainly influenced by the immediate adsorption of Pl on cement particles, increased with an increase in the dosage of Pl. Slump loss or decrease of concrete flowability with time, which is determined by the hydration process of the cement, the content of SO_3, alkali content, C-S-H-bridge formation, also depends on Pl type. The researchers established that carboxylic acid-based plasticizer is more effective in improving flow properties in comparison with LS, SNF and SMF. Zhang *et al.* (2010) investigated the effect of newly developed LS on the loss of flowability of cement pastes. They identified that cement pastes modified by new developed LS lost flowability more slowly in comparison with PCE and NF.

It should be noted that the method of addition of Pl plays a crucial role in concrete technological properties and hydration. Uchikawa *et al.* (1995) established that flow and slump loss of cement paste prepared by latter addition of tested admixture, such as polycarboxylic acid-based, β-naphthalenesulfonic acid-based and lignin sulfonic acid-based admixtures are higher than it is with simultaneous addition. The Fig. 1.3 shows the changes in the flow of cement pastes depends on the type of Pl, method of addition and time. The authors explained the improvement of the flowability of cement paste by latter addition in view of the significant reduction of the amount of admixture adsorbed to tricalcium aluminate phase.

With increasing interest to the HWC and SCC, the flowing speed of fresh concrete mixture is an essential factor as well. Lange *et al.* (2014) paid attention to the fact that the application of PCE with low W/C, less than 0.40 led to sticky, viscous and honey-like consistency, creeping flow behaviour which is not suitable for pumping, placement and compaction of concrete. The researchers investigated a model which explains the unique flow characteristics of mortar and concrete called a flow speed-enhancing effect. They showed the dependence between this flow model and the hydrophilic-lipophilic balance (HLB) of PCE. The current research demonstrated that PCE molecule must be as hydrophilic as

possible, hydrophobic groups such as $–CH_3$ should be avoided to reach a high speed of flow. Moreover, Lange *et al.* (2014) established that dispersing ability of PCE does not depend on HLB.

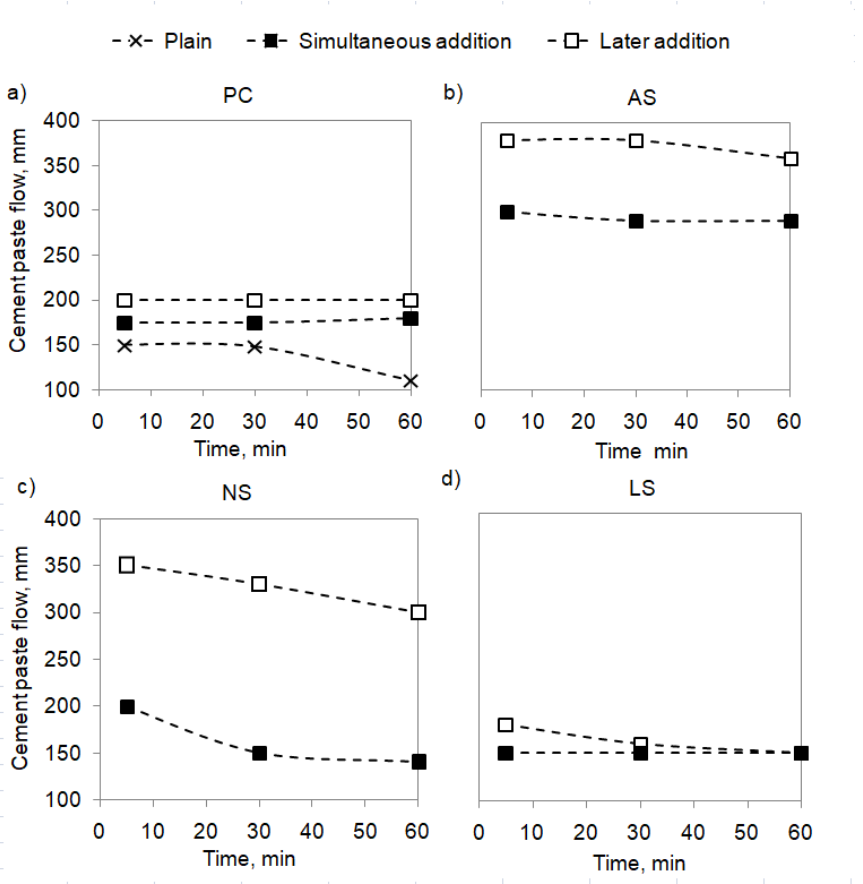


Fig. 1.3. The dependency of cement paste flowability on type of plasticizing admixture, method of its addition and time for: a) PC – polycarboxylate; b) AS – aminosulfonate; c) NS – naphthalene sulfonate; d) LS – lignosulfonate plasticizers (Uchikawa *et al.* 1995)

Application of Pl determines the hydration properties and setting time of cement-based materials. Zhang *et al.* (2010) investigated the effect of newly developed LS on the initial setting time of cement pastes and compared it with PCE and NF. They identified that cement pastes modified by new developed LS had longer initial setting time in comparison with PCE and NF plasticizers.

Authors highlighted that all observed Pl retard the cement hydration, but the degree of retardation depends on the type and dosage of Pl. The curves of the heat evolution of cement pastes with Pl studied in this research are shown in Fig. 1.4.

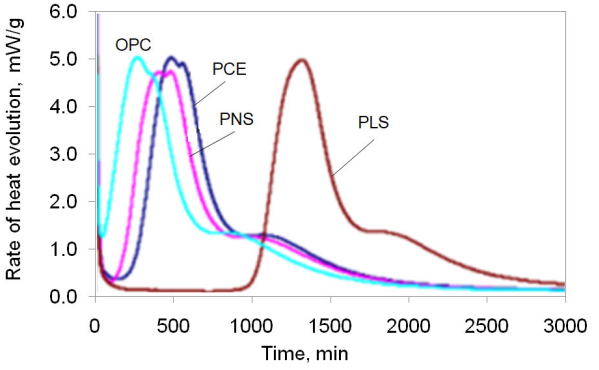


Fig. 1.4. Rate of heat evolution of cement pastes with water to cement ratio 0.26 and different plasticizing admixtures: OPC – ordinary Portland cement; PLS – lignosulfonate; PCE – polycarboxylate; PNS – polynaphthalene plasticizers (Zhang *et al.* 2010)

A lot of modern researches demonstrated the changes in hydration of cement-based materials modified by different types of Pl. For example, Danner *et al.* (2016) investigated the hydration of C_3A-gypsum paste with Ca- and Na-lignosulfonate (CLS and NLS) in a concentration of 1 and 4%. The research results showed the absence of C_3A retardation and ettringite formation with 1% CLS and NLS. The increase of Pl dosage up to 4% led to the small retardation of C_3A and absence of retardation in ettringite formation. The authors highlighted the crucial role of sugar content in LS as the main reason for the retardation effects.

Wang *et al.* (2012) studied the effect of calcium LS on the hydration of Portland cement containing anhydrite. Usage of LS led to quick set caused by the accelerated reaction between C_3A and the anhydrite at the initial hydration time. Addition of LS promotes the decrease of SO_4^{2-} concentration and $CaSO_4$ saturation ratio whereas Ca^{2+} concentration increases. The authors of current research observed that modification of cement-based material by LS contributes to the acceleration of the ettringite formation caused by the decrease of $CaSO_4$ saturation ratio. Dalas *et al.* (2015b) investigated the early C_3A-$CaSO_4$ hydration with different amounts of two PCE in different grafting degree. They concluded that PCE increases the ettringite specific area for a variable period. However,

this increase depends on the charge and dosage of PCE. Emoto & Bier (2007) noticed the retardation effect in the cement-based materials caused by the addition of PCE plasticizer.

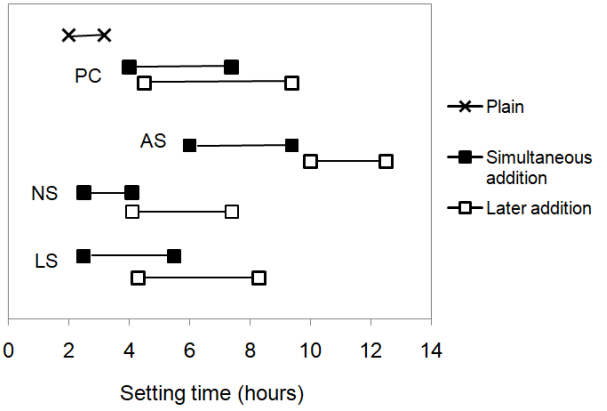


Fig. 1.5. The dependency of cement paste setting time on type of plasticizing admixture and its addition method for: PC – polycarboxylate; AS – aminosulfonate; NS – naphthalene sulfonate; LS – lignosulfonate plasticizers (Uchikawa *et al.* 1995)

The addition time of Pl affected on the setting time of cement pastes as well (Uchikawa *et al.* 1995). The researchers identified that the retardation and difference between the initial and final setting time of cement pastes prepared by later addition of Pl admixtures were more significant than those by simultaneous addition. The influence of the addition method of Pl on the setting time of cement pastes is presented in Fig. 1.5.

Mainly, the addition of Pl to cement-based materials lead to the retardation of hydration processes. The technological properties and hydration of cement-based materials with Pl are determined primarily by compatibility between binders, mineral additives and chemical admixtures.

Hanehara & Yamada (1999) investigated the problem of incompatibilities between cement and chemical admixtures, which may be the reason for stiffening (pseudo-setting), large slump-loss or remarkable retardation of setting. The researchers observed different kinds of Pl, such as LS, PNS, MS, AS and PCE. They established that PCE has better compatibility with different types of cement in comparison with other admixtures. The compatibility between Pl and cement was studied by Nagrockiene *et al.* (2013) and Msinjili *et al.* (2017) as well. The retardation of cement hydration is a more undesirable effect which

takes place in the course of modification of cement-based materials by Pl. Moreover, the mechanisms which cause the retardation are not profoundly investigated and require the clarification. In real practice, the commercial Pl contain defoamers, accelerators, viscosity-modifying admixtures which get the opportunity to manage by retardation effect. Nowadays, the researchers explain the retardation effect by the complexation of calcium ions, slowing down of dissolution of anhydrous phases, disrupting nucleation of hydrates and perturbation of the aluminate-silicate-sulfate balance (Aitcin & Flatt 2016b).

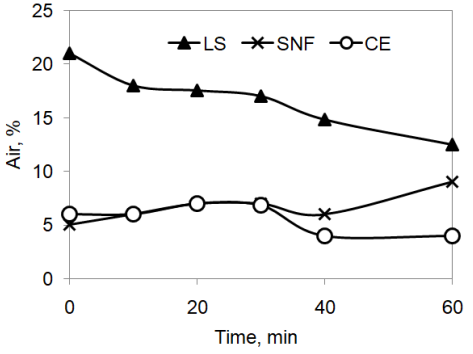


Fig. 1.6. Amount of air in cement mortar with different plasticizing admixtures: SNF – naphthalene formaldehyde sulfonic acid; CE – polyacrylic acid polymer; LS – lignosulfonic acid (Chandra & Bjornstrom 2002)

Water bleeding, sedimentation and air-entraining are the essential factors which should be taken into account in managing by the technological properties of concrete with Pl. Development of SCC requires to control the amount of entrained air as well. Lazniewska-Piekarczy (2014) highlighted the necessity of Pl compatibility test to verify the air-entrainment effect. The correlation between the results of surface tension test of different Pl solutions and air-content in SCC was established. Chandra & Bjornstrom (2002) demonstrated that LS entrains air to a greater extent than other types of studied Pl in view of the presence of surface-active agents. The graphs of air content with different kinds of Pl are presented in Fig. 1.6.

Addition of Pl to the cement-based materials requires paying attention to the stability of cement-based materials, which is correlated with rheological and technological properties (Mikanovic & Jolicoeur 2008; Peng *et al.* 2013; Peng & Jacobsen 2013). Mikanovic & Jolicoeur (2008) studied the effect of NF and PCE on rheology and stability of cement pastes. They established that the presence of Pl enhance water bleeding and sedimentation when the flowability

of cement pastes with both Pl are similar. Peng *et al.* (2013) investigated the sedimentation and water bleeding of cement pastes with LS. They obtained that LS generally prolonged the sedimentation process and decreased bleeding rates. The researchers highlighted that different type of LS showed a distinct influence on water bleeding and sedimentation. Han & Wang (2016) highlighted the importance to control the water bleeding of cement pastes due to its further impact on properties of cement composites in the hardened state. The researchers identified the increase of porosity, changes in hydration products, mechanical properties and anti-penetration ability of hydrated cement paste with the increase in water bleeding. The evaluation of performance characteristics and microstructure of concrete with Pl was observed by Huang *et al.* (2016). The researches compared the cement pastes with PCE and NF and their influence on concrete durability. The authors revealed that cement pastes with PCE have more hydration products and a higher ratio of high-density C-S-H to low-density C-S-H, which have further influence on microstructure and mechanical properties. The PCE showed a better microstructure of concrete in comparison with NF plasticizer.

The understanding of retardation mechanisms of Pl, managing by the amount of entraining air, water bleeding degree, flowability in cement-based materials will allow managing by the properties of HWC and SCC.

1.3. The Methods of Homogenization of Nanoparticles in Aqueous Suspension and Cement-Based Materials

The modification of cement composites by nanoparticles (in particular, by CNT studied in the current research) is based on two stages, which consist of suspension preparation and introduction of nanoparticles suspension in the cement matrix (Rashad 2017; Bogas *et al.* 2019).

The tendency of nanoparticles to the agglomeration hinders their wide usage in construction practice. It requires the special methods for more efficient homogenization in water suspension and the cement-based materials. The different methods are applied nowadays to solve the problem with the homogenization of nanomaterials in the dispersion medium, such as ultrasonication, high shear mixing, methods which alter the surface chemistry of nanoparticles covalently by their functionalization and non-covalently by adsorption of some chemical dispersants. Different methods have the advantages and disadvantages, which can influence the further properties of nanomodified cement composites

(Rashad 2017; Bogas *et al.* 2019; Vaisman *et al.* 2006; Hilding *et al.* 2003; Ma *et al.* 2010).

Ultrasonication of nanoparticles suspension is one of the more widely used homogenization methods. This method is based on the propagating through the dispersion medium the ultrasonication waves which cause the periodical compression and rarefaction. The compression and rarefaction cause the formation of microbubbles, which violently collapse after reaching a critical size with the further occurrence of cavitation processes. The collapse of microbubbles promotes the formation of extreme conditions with a local temperature about 5000 K, pressure above 500 bars and the appearance of powerful hydromechanical shear forces and the oxidizing effect of H– and –OH. The hydromechanical shear forces in combination with oxidizing effect ensure the breakup of dispersible particles. The ultrasonic bath or ultrasonic probe/horn are more widely applied in laboratory condition. The images of the ultrasonic bath, ultrasonic probe are presented in Fig. 1.7 (Guangyin & Zhao 2016).

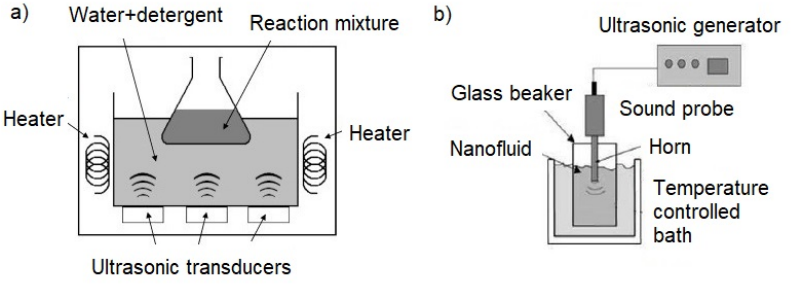


Fig. 1.7. Scheme of ultrasonication equipment: a) water bath sonicator; b) probe/horn ultrasonicator (Sajumon *et al.* 2013; Kwitkowska *et al.* 2011)

The number of researches describes the application of ultrasonication for the homogenization of CNT suspension. The scientists highlight that the efficiency of CNT ultrasonication is determined by its intensity, duration, type of applied dispersing agent, compatibility between a dispersing agent and CNT and some other parameters. The efficiency of CNT ultrasonication has a further impact on the properties of cement composites. Zou *et al.* (2015) investigated the effect of ultrasonication energy on the engineering properties of ordinary Portland cement paste modified by CNT suspension. The researchers established that higher ultrasonication energy is required to reach a better CNT suspension. The ultrasonication of CNT was performed in the presence of Pl. The Pl to CNT ratio was established as 1 to 8. The best mechanical properties of cement composites modified by CNT was gained at the ultrasonication energy of 50 J/mL. Jaro-

lim *et al.* (2016) noticed the necessity of an appropriate quantity of ultrasonic energy and compatible surfactant for the better homogenization of CNT suspension. The energy of 800 J/ml was established as optimal in the medium of naphthalene based Pl. Chen *et al.* (2016) studied the agglomeration process of CNT which are homogenized by ultrasonication for 10 min with naphthalene and lignosulfonate based Pl in saturated $Ca(OH)_2$ solution. The researcher proposed the agglomeration model of CNT suspensions and revealed that small CNT bundles are more stable than individual tubes. Not only Pl determines the properties of suspension, but also type of CNT. Krause *et al.* (2010) demonstrated the changes in properties of CNT suspensions prepared with different types of CNT at various ultrasonication treatment times. The ultrasonication of CNT suspension is linked with the problems of their shortening during the treatment which may affect the further properties of cement composites. Chen *et al.* 2014 established that an increase of ultrasonication time leads to a decrease in the reinforcing efficiency of CNT. They identified the optimal ultrasonication energy of 89 J/ml. Alrekabi *et al.* (2016) prepared the CNT suspension in combination with PCE as a dispersing agent at an intensive and moderate sonication intensity. They observed that longer duration of ultrasonication at moderate intensity leads to the breaking of nanotubes. Intensive sonication for 5 min showed the considerable increment in concentration of individually dispersed tubes in water.

In addition to the ultrasonication, homogenization of CNT in dispersion medium by the hydrodynamic cavitation technique demonstrated the effective distribution of CNT. Gusev & Petrunin (2014) used the cavitation method for homogenization of CNT. The scheme of a hydrodynamic cavitation device is presented in Fig. 1.8.

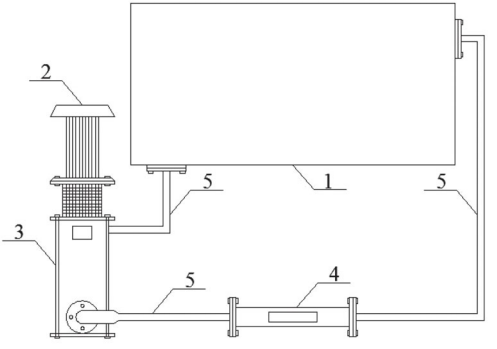


Fig. 1.8. Scheme of hydrodynamic cavitation device: 1 – working container for receiving a solution; 2 – 3 kW electric motor; 3 – multi-stage and multi-core pump; 4 – passive hydrodynamic dispergator; 5 – connecting elements (Gusev & Petrunin 2014)

The action mechanism of such method consists of a reagglomeration of CNT by cavitation effects. The cavitation effects appear in the course of fluid flow through a specially designed cavitator channel, which causes the generation of gas and steam-gas bubbles. The collapses of bubbles cause the intense shock-wave processes with the appearance of zones with ultra-high pressure and temperatures. These processes lead to the uniform homogenization of CNT in the volume of water suspension. The authors highlighted that cavitation method is more suitable in comparison with ultrasonication in terms of industrial production, which requires less energy consumption. Yakovlev *et al.* (2014) established that the usage of a hydrodynamic cavitation device leads to the improvement of the mechanical properties of autoclaved aerated gas silicate modified by homogenized CNT suspension.

The high shear mixing methods are used to disperse CNTs, especially, in the polymer matrix. These methods are based on the stirring with high intensity. The rotor-stator with moving rotor and stationary stator is an example of high shear mixing equipment. The high speed and minimal gap between the rotor and stator provide the generation of strong shear forces which lead to the homogenization of particles (Ma *et. al.* 2010). The scheme of rotor-stator is presented in Fig. 1.9.

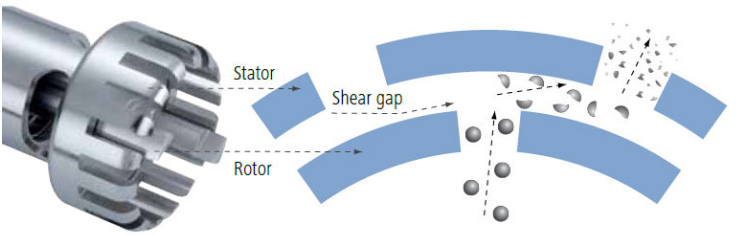


Fig. 1.9. Scheme of rotor-stator (Technical data sheet on IKA dispersers)

To grind the materials into an extremely fine powder of the nanometer size around of 100 nm, the ball milling method is used (Munkhbayar *et al.* 2012; Munkhbayar *et al.* 2013; Piao *et al.* 2017). The method is based on the local generation of high pressure caused by the collision between the tiny and rigid balls in a concealed container. The scheme of the planetary ball mill is presented in Fig. 1.10 (Ma *et. al.* 2010).

Munkhbayar *et al.* (2012) studied the effect of ball milling on the dispersibility of MWCNTs suspension. The decrease in agglomerated size of CNT was reached with an increase of rotation speed. The authors noticed that the further

increase of grinding speed may lead to the further separation of CNT into individual nanotubes. Besides, the researchers obtained that the wet grinding at a rotation speed of 500 rpm in combination with ultrasonication enables to reach the better dispersion characteristics (Munkhbayar *et al.* 2013).

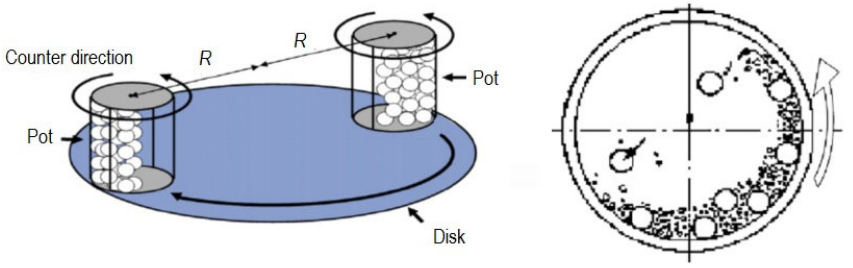
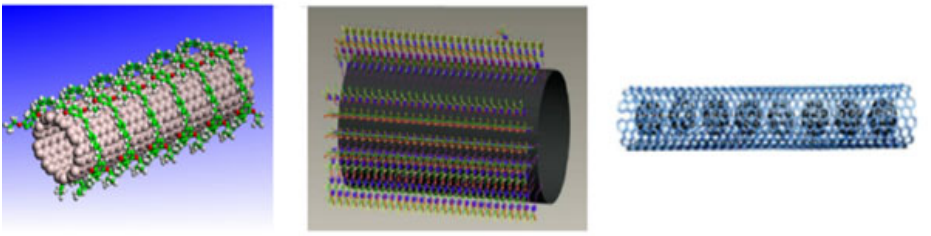


Fig. 1.10. Scheme of planetary ball mill (Ma *et. al.* 2010; Munkhbayar *et al* 2013)

The disentangling of bundled CNT into individual may be performed by magnetic field induction method (Son *et al.* 2017), dielectrophoresis method (Dimaki & Boggild 2004) and some others. However, these methods found the more widespread application in the field of electronics.

In addition to mechanical methods, the covalent and non-covalent functionalization of CNT is used as an effective method of homogenization. The covalent functionalization is provided by two methods, such as direct covalent sidewall functionalization and defect functionalization. The first method is based on the change of hybridization of C atoms from sp^2 to sp^3 in the presence of molecules with high chemical reactivity. The second one is associated with the stabilization of CNT defects by bonding with hydrophilic polar groups, such as carboxylic acid or hydroxyl groups.

The non-covalent functionalization method involves polymer wrapping, surfactant adsorption and endohedral methods. The endohedral method consists in the insertion of guest atoms or molecules in the inner cavity of CNT through the capillary effect. The surfactant adsorption method is based on the application of non-ionic, anionic or cationic surfactants. The surfactant adsorption on the CNTs decreases the surface tension, overcome the van der Waals attractions via electrostatic/steric repulsive forces and, as consequence, prevents the formation of aggregates. The wrapping of polymer around of CNT is provided through the van der Waals interactions and π–π stacking between CNT and polymer chains and leads to the formation of supermolecular complexes of CNT. The non-covalent functionalization of CNT is presented in Fig. 1.11 (Ma *et. al.* 2010).



a) b) c)

Fig. 1.11. Non-covalent funcionalization of carbon nanotubes: a) polymer wrapping; b) surfactant adsoprtion; c) endohedral method (Ma *et. al.* 2010)

The number of researches is devoted to the covalent and non-covalent CNT functionalization. For example, Liu *et al.* (2017b) used three types of Pl, such as cationic, anionic and nonionic as a dispersing agent. The optimal result of CNT homogenization was obtained with a cationic surfactant, the ratio between surfactant and CNT of 5:1 at optimal ultrasonic time of 120 s. Moreover, the authors observed that CNT with more carboxyl groups have a better dispersion in water. The better efficiency of the cationic surfactant in comparison with anionic and non-ionic surfactants was established by Ramos *et al.* 2017. Cui *et al.* 2017 highlighted the importance of the chemical molecular structure of surfactant on the efficiency of MWCNT distribution. Liebscher *et al.* 2017 investigated the effect of the molecular architecture of PCE on the homogenization of CNT. The researchers established that PCE with long backbone and high side-chain density is more efficient in comparison with lower side-chain densities and short backbones.

Petrunin *et al.* (2015) used a covalent functionalization method of CNT by oxygen-containing functional groups and noticed that CNT promotes the acceleration of the hydration processes in cement composites. Li *et al.* (2005) treated the MWCNT by H_2SO_4 and HNO_3 and did not use some mechanical homogenization techniques for distribution of nanotubes. Fuge *et al.* (2016) studied the homogenization of undoped and nitrogen-doped MWCNT under ultrasonication treatment. The authors observed that higher ultrasonication amplitude leads to the length-reduction of the MWCNT and the length-reduction for nitrogen-doped MWCNTs is more remarkable in view of a weaker chemical bond between C and N in CNT-lattice in comparison with bonds only between carbon atoms.

For better distribution of nanoparticles in aqueous suspension and cement matrix, the combination of mechanical and chemical methods is applied. The combined application of ultrasonication treatment and chemical admixtures is a

commonly used method of nanoparticles distribution (Sobolkina *et al.* 2012, Bogas *et al.* 2019). Du *et al.* (2017) observed the effect of methylcellulose on the properties of CNT suspension and cement composites. The increase of suspension stability, a decrease of cement pastes water bleeding and improvement of strength properties of nanomodified cement composites were observed at the range of methylcellulose from 0.10 to 0.20 wt% and the application of ultrasonication technique for CNT homogenization.

The effective distribution of nanoparticles can be gained in case of addition of micro-particles. For example, Kim *et al.* (2018) studied the influence of Pl and silicious materials on the homogenization of CNT. The authors established that ultrasonication in the presence of PCE and micro-silica effectively disperses the CNT in cement-based materials. Taha *et al.* (2020) proposed the ultrasonication of CNT suspension in combination with clay micro-particles which led to the reagglomeration and stabilization of suspension.

To achieve better embedding of CNT in the cement matrix different synthesis methods are used. Sobolkina *et al.* (2014) deposited silica on the sidewall of CNT by a sol-gel method. Sikora *et al.* (2019) covered CNT by silica core-shell structures to improve the binding ability of CNT to cement matrix and enhance the strength properties of cement composites. Nasubulin *et al.* (2013) proposed the novel approach of the CNT growth directly on the surface of the matrix, matrix precursor or filler particles. The composites modified by CNT generated in this method showed the enhancement of mechanical and electrical properties.

The researches described above confirm the efficiency of mechanical and chemical CNT homogenization methods. The combination of different techniques contributes to the better CNT distribution in aqueous suspension and leads to the further improvement of cement composites modified by them.

1.4. The Influence of the Nanoparticles on the Characteristics of Cement-Based Materials

Modification of cement-based materials by nanoparticles and nanostructures enables to manage by the structure of materials on the atomic level and, as a consequence, to obtain the materials with unique properties.

Several methods are used to obtain nanostructures with different parameters. The classification of methods according to the changes in particle size in the course of synthesis is more widely used. This classification includes the "top-down" approach, which is based on the reduction of structure size to the nanoscale level, and "bottom-up" approach, which characterizes the engineering of materials from atoms or molecular components through a process of assembly or self-assembly (Sanchez & Sobolev 2010).

The dependence between specific surface area, size of particles and type of produced concrete is presented in Fig. 1.12 (Sanchez & Sobolev 2010).

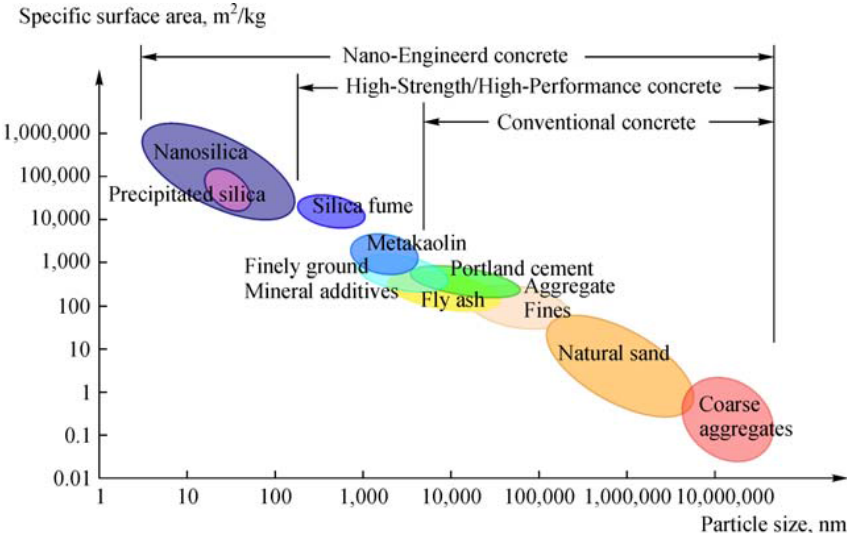


Fig. 1.12. Dependence between particle size, specific surface area and type of generated concrete (Sanchez & Sobolev 2010)

A considerable number of researches demonstrate the improvement of the performance characteristics of cement-based materials in a fresh and hardened state in the course of their modification by different types of nanoparticles and nanostructures, such as nano-SiO_2, nano-TiO_2, nano-Fe_2O_3, nano-Al_2O_3, nano clay etc.

Modification of cement-based materials by nano-SiO_2 enables to manage by their properties in a fresh state, hydration kinetics, mechanical properties and durability (Senff *et al.* 2009; Hou *et al.* 2015; Said *et al.* 2012; Zhang *et al.* 2017; Ghafari *et al.* 2014). The decrease of spread diameter by 19.6% and the increase in yield stress and plastic viscosity by 157% and 3.6%, respectively, were obtained in the course of modification of cement mortar by 2.5% bwoc of nano-SiO_2 (Senff *et al.* 2009). Addition of nano-SiO_2 increases the hydration processes of cement at an early age and decreases it at a later age due to the compact structure of the pozzolanic hydration products of nano-SiO_2 (Hou *et al.* 2015). Pozzolanic reaction and filler effect of nano-SiO_2 in cement matrix promotes the improvement of mechanical properties and durability of cement composites. Said *et al.* (2012) established the significant decrease of the

total porosity and the threshold pore diameter of the cement matrix by the usage of nano-SiO_2 in the dosage up to 6%. Moreover, the addition of nano-SiO_2 significantly decreases the water absorption capacity and reduce the chloride migration and diffusion coefficient (Zhang *et al.* 2017).

Nano-TiO_2 is used as a component of "self-cleaning" and "de-polluting" concrete (Sanchez & Sobolev 2010). Its application in concrete decreases the water absorption, chloride permeability and noticeably improve the electrical resistivity (Mohseni *et al.* 2015).

Addition of nano-Fe_2O_3 to concrete allows obtaining concrete with self-sensing properties (Sanchez & Sobolev 2010). Li *et al.* (2004) observed that modification of cement mortar by nano-Fe_2O_3 enhance the flexural and compressive strength by 22% and 21.8%, respectively.

Modification of cement matrix by nano-Al_2O_3 leads to the formation of denser structure (Barbhuiya *et al.* 2014; Rashad 2013) and promotes to the decrease the crack width when plain rebars are used in concrete (Ismael *et al.* 2016).

The number of researches demonstrates the improvement of mechanical properties and durability of concrete modified by nano-$CaCO_3$ (Wu *et al.* 2016; Li *et al.* 2015). Wu *et al.* (2016) established the optimal dosage of nano-$CaCO_3$ from 1.6% to 4.8%, which led to an increase in compressive and flexural strength.

As it is obvious based on the researches mentioned above, the addition of nano-SiO_2, nano-TiO_2, nano-Fe_2O_3, nano-Al_2O_3 to cement matrix leads to the decrease of flowability of cement-based materials in a fresh state, significantly increase the mechanical properties and improve the durability of cement composites in view of their ability to nucleation, filling effects and generation of less porous and more homogeneous structure.

Moreover, considerable attention of researchers is paid to the modification of cement matrix by carbon nanomaterials, such as CNT, nanofibers (CNF), nano graphite platelets (GNP). Addition of carbon nanomaterials in some hundredths of a per cent by weight of cement provides the improvement of rheological and technological properties, performance and durability of cement-based materials. For example, Meng & Khayat (2016) established that GNP in a dosage of 0.3% bwoc increases the flexural strength of ultra-high-performance concrete by 59%. Also, the researchers observed that the increase of GNP from 0 to 0.3% increase the air content in concrete mixture by 20–30%.

In addition to GNP, Meng & Khayat (2016) studied the effect of CNF on concrete. The 0.3% of CNF enhanced the flexural strength by 46% and increase amount of air in concrete mixture by the same value.

The significant attention of researchers is paid to the modification of cement composites by CNT in view of their outstanding mechanical, thermal, opti-

cal, electrical and other properties. CNT present the one-dimensional carbon materials with an aspect ratio greater than 1000, which were firstly observed by Iijima in 1992 (Shunin et al. 2018).

CNT are cylinders consisting of rolled-up graphite planes with diameters of nanometer scale. One end of CNT frequently is capped by a hemisphere of fullerene structure. CNT may consist of a single graphene layer and two or more concentric cylindrical shells of graphene sheets which are coaxially arranged around a central hollow with Van der Waals forces between adjacent layers. These CNT called single-walled (SWCNT) and multi-walled CNT (MWCNT), respectively. The rolling angle of the graphene sheet determines the properties of CNT, mainly, electrical properties. Depending on the rolling angle, CNT classified into the armchair, zigzag and chiral type. The structure of CNT according its chilarity is shown in Fig. 1.13 (Rafiei 2015; Shunin *et al.* 2018).

The sp^2 chemical bonds of carbon atoms in CNT, which are stronger than sp^3 bonds, promote the higher strength and modulus of CNT (Liew *et al.* 2016).

Nowadays, the synthesis CNTs is carried out by methods of arc discharge, laser ablation and chemical vapour deposition to produce a significant amount of CNT with required purity.

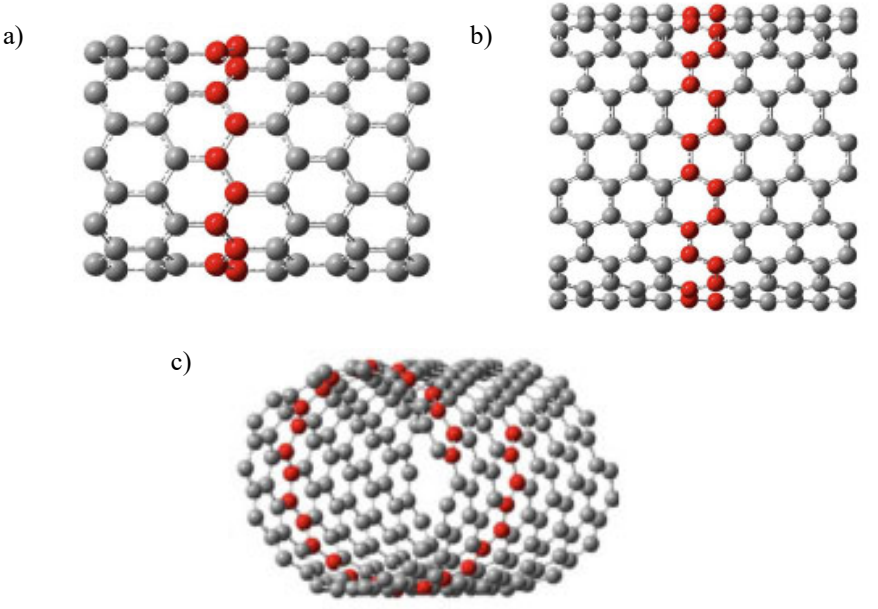


Fig. 1.13. Structure of carbon nanotubes: a) zigzag; b) armchair; c) chiral type (Shunin *et al.* 2018)

The chemical vapour deposition method (CVD) is one of the promising approaches for large-scale production of CNT. Hydrocarbon gases such as carbon monoxide (CO), acetylene (C_2H_2), methane (CH_4) and benzene (C_6H_6) are used as carbon sources. Further, the hydrocarbon gases flow through the quartz tube with heating to 600–1200 °C inside the furnace. Argon is applied as flow gases. Passing the hydrocarbon vapour through a quartz tube takes 60 min. The metal catalyst, such as Fe, Ni and Co outside the furnace initiates self-organization processes of carbon. Also, catalyst material can be placed inside the furnace and provides the condensation of atomized carbon with growing certain form of CNT (Shunin *et al.* 2018).

Addition of CNT to cement composites allows managing by the properties of cement-based materials in a fresh and hardened state (Reales *et al.* 2018; Jiang *et al.* 2018; Ma *et al.* 2018). For example, Reales *et al.* (2018) investigated the rheological properties of cement pastes modified by MWCNT/surfactant aqueous dispersions and revealed the shift to higher yield stress values while maintaining viscosity on the same level caused by a modification of the interparticle attractions. Jiang *et al.* (2018) identified the increase in yield stress of cement pastes modified by CNT and explained it by high specific surface area and intertwining effect of nanoparticles.

The majority of researchers revealed the increase of mechanical parameters of nanomodified cement composites (Lee *et al.* 2018; Metaxa *et al.* 2012; Li *et al.* 2015). For instance, Xu *et al.* (2015) observed the enhancement of compressive strength of cement paste by 22% and 15% with the addition of MWCNT in the dosage of 0.1% bwoc at 7 and 28 days, respectively. Al-Rub *et al.* (2012) investigated the mechanical properties of cementitious nanocomposites depending on the length of CNT. They obtained the increase in flexural strength by 269% and 65%, respectively, for short 0.2% bwoc MWCNT and long 0.1% bwoc MWCNT. According to Carrico *et al.* (2018), the modification by 0.05–0.1% CNT bwoc improves the strength and durability properties up to 21% and 25%, respectively. The obtained results were correlated with the nucleation and bridging effects of CNT observed by SEM. Rocha *et al.* (2019) received that the presence of CNT up to 0.1% bwoc increases the fracture energy by 90%, flexural strength by 46% and tensile strength by 47%.

The number of researches shows the enhancement of microstructure, decrease of total porosity and improvement of pore diameter distribution in cement composites modified by MWCNT (Xu *et al.* 2015; Al-Rub *et al.* 2012; Han *et al.* 2015; Melo *et al.* 2011; Cui *et al.* 2017; Yakovlev *et al.* 2014). Alafogianni *et al.* (2019) established that small amounts of CNT up to 0.4% bwoc reduce cement mortar sorptivity up to 50%, due to the refinement of pores in the mortar.

In addition to the changes in rheological, mechanical properties and microstructure of cement composites, unique electrical properties of MWCNT can be used for generation of smart strain sensing cement composites (Luo *et al.* 2018; Ubertini *et al.* 2014; Kim 2015). For example, Pisello *et al.* (2017) investigated the effect of MWCNT on cement-based composites in terms of optical features, thermal characteristics, electrical properties and strain-sensing capability. Researchers observed that MWCNT are efficient in providing the material with strain-sensing capabilities and in protecting its surface against the damaging UV-rays. Konsta-Gdoutos *et al.* (2014) found that nanocomposites reinforced with 0.1% bwoc CNT exhibited an increased change in resistivity, which is indicative of the amplified sensitivity of the material in strain sensing. Nam *et al.* (2018) fabricated an electromagnetic wave absorber based on MWCNT-incorporated cement composite.

However, the application of CNT in construction practice is limited in view of agglomeration processes which take place in the process of homogenization of MWCNT suspensions and their distributions inside the cement-based materials (Hongyu *et al.* 2017). The problems with the homogenization of CNT can lead to the absence of enhancement or the decrease of cement composites performance. The researchers are searching for the suitable homogenization method for equal distribution of CNT in aqueous suspension and cement-based materials. For example, Lee *et al.* (2019) compared the addition of MWCNT in a solution and powder form. In this research, the cement composites with MWCNT in powder form showed the worse strength properties caused by agglomeration processes. Isfahani *et al.* (2016) observed the absence of improvement in flexural and compressive strength of cement mortars either by increasing the amount of CNT or imposing sonication of CNT in mixing water. Also, the researchers identified the insufficient bonding between CNT and hydration products, which could also contribute to the lack of mechanical improvement.

The addition of nanoparticles and nanostructures into cement-based materials have a significant effect on their properties in a fresh and hardened state. The application of small dosages of nano additives is a promising tool in managing by the properties of cement-based materials. Nevertheless, the usage of nano additives in cement-based materials requires a further understanding of their action mechanisms and searching for effective methods for their homogeneous distribution into cement-based materials.

1.5. The Technological Properties of the Cement Mixtures Modified by the Nanoparticles

As it was mentioned above, nanoparticles and nanostructures have a significant effect on the properties of cement-based materials in a fresh and hardened state. The number of researches confirms the impact of nano additives on technological properties, however the action mechanisms of nano additives remain not clear enough. Therefore, the investigation of the effect of nanoparticles and nanostructures on the cement-based materials requires further observation.

Modification of cement-based materials by nanoparticles such as nano-SiO_2, nano-TiO_2, nano-Al_2O_3 has a great interest of researchers in view of their significant potential in managing by the technological properties of cement-based materials (Senf *et al.* 2012; Xiao *et al.* 2019; Kawashima *et al.* 2013). For example, Senf *et al.* (2012) investigated the cement pastes and mortars modified by nano-SiO_2 and nano-TiO_2 in terms of rheological and technological properties. In the course of experiments, the researchers observed the significant increase of values of torque, yield stress, plastic viscosity and the reduction of flow table values.

Xiao *et al* (2019) studied the effect of pozzolanic and non-pozzolanic nanomaterials on the properties of cement-based materials. The research demonstrated the decrease of the fluidity of cement paste in the case of modification by nanomaterials, such as pozzolanic nano-SiO_2 and non-pozzolanic nano-TiO_2. The fluidity decreases in greater extent with an increase of the nano-material content and decrease of its size. The addition of nano-SiO_2 in the dosage of 0.5% bwoc with a size of 15 nm reduced the fluidity of cement paste by 58.3%. The increase of the nano-SiO_2 content up to 3% led to the total loss of cement paste fluidity. The modification of cement paste by nano-TiO_2 showed better fluidity for the same dosage and size of nano-TiO_2 in comparison with nano-SiO_2. The researchers highlighted that content of nanomaterials should be less than 3% bwoc to avoid the significant decrease in fluidity.

The decrease in flowability of the mixture was observed by Bolhassani &Samani (2014) as well. The nano-SiO_2 with a specific surface area more than 150 m^2/g and dosage more than 3% promotes the loss of mixture workability.

Zhang *et al.* (2015) conducted research on the topic of modification of cement-based materials by nano-TiO_2. The researchers confirmed the results of investigation of other researchers when the reduction in the fluidity of cement mortar of 2.8%, 19.8%, 20.8% in the used dosage of nano-TiO_2 of 1%, 3% and 5%, respectively, was observed.

It is important to note that the modification by carbon nanomaterials, such as GNP, CNF and CNT require a detailed investigation in terms of influence on technological properties as well.

The modification of cement-based materials by graphene leads to the reduction of workability of cement pastes (Pan *et al.* 2015; Kjaernsmo *et al.* 2018). Pan *et al.* (2015) performed the mini-slump test of cement paste with and without graphene oxide (GO) and established the reduction of workability by 41.7% with the addition of GO in the dosage of 0.05% bwoc. The obtained results were explained by the large surface area of the graphene sheet, which decreases the available water in the fresh mix in view of wetting of graphene sheets. Kjaernsmo *et al.* 2018 obtained that increasing content of GO from 0.03% to 0.2% bwoc leads to the reduction of workability of cement mortar. In addition to workability changes, it is essential to note the effect of GO on the air content of cement mortar. The researchers observed the increase in air content from 3.2% to 4.9% in the case of a modification of cement mortar by 0.2% bwoc of GO. The amount of air affects poor compaction and workability. In view of this fact, it is necessary to pay attention to the amount of air in cement mixtures, however the number of researches devoted to this issue is not significant.

Meng & Khayat (2018) presented that an increase in the dosage of CNF from 0.1% to 0.3% bwoc leads to an increase in the adsorption effect of the nanomaterials and decrease of flowability. Addition of CNF in the dosage from 0 to 0.3% bwoc increases the amount of air in ultra-high performance concrete from 2.5 to 3.2%.

Tolmachev & Belichenko (2014) studied the modification of cement paste by carbon nanoparticles with a size of $10^{-7}...10^{-8}$ m generated by ultrasonication of coke dust in the water. According to the special methods of cone spreading under vibration, the researchers obtained that introduction of carbon nanoparticles in the dosage of 0.0225% bwoc led to the increase in cone spreading from 11.2 cm to 14 cm in comparison with reference sample without admixtures.

It is vital to note that the significant attention of researchers is paid to the modification of cement-based materials by CNT. The influence of CNT on the technological properties of cement-based materials is correlated with the effect of other types of nanomaterials. Mostly, the introduction of CNT decreases the workability of cement mixtures, however the impact of CNT is dissimilar in some cases. Therefore, the researches on the effect of CNT on technological properties of cement-based materials are still relevant.

Konsta-Gdoutos *et al.* (2017) investigated the effect of CNT on the properties of cement mortar in a fresh and hardened state. The authors revealed that addition of pristine CNT with different aspect ratio in the dosage of 0.1% bwoc leads to the decrease in flowability. The maximum changes of flowability were achieved when it was decreased from 22.1 cm to 18.6 cm.

Collins *et al.* (2012) performed the mini-slump test of ordinary cement pastes in different W/C ratio modified by the various dosages of CNT. The spreading diameter of cement paste decreased by 14.5% with the addition of

0.5% bwoc of CNT at W/C ratio of 0.5. The other dosages of CNT and other W/C ratio showed the decrease in flowability of cement pastes as well. The authors of the research noticed the importance of the selection of chemical admixture which can be used as a dispersing agent for CNT suspension and can manage by the properties of cement-based materials in a fresh and hardened state.

Parveen *et al.* (2015) reinforced the cement composites by MWCNT suspension prepared with surfactant and defoaming agent. The consistency tests revealed that CNT did not cause significant changes, as opposed to the researches mentioned above.

According to Alatawna *et al.* (2020), all carbon-based nanofillers, including CNT, decrease workability of a cement mixture.

Li *et al.* (2019) observed the decrease in flowability of magnesium phosphate cement modified by CNT and explained the observed changes by bridging, pore-filling and nano-size effects of CNT in the cement matrix.

In addition to the effect of nanomaterials on the flowability, it is essential to pay attention to their impact on the amount of air in cement-based materials, water bleeding and segregation. For example, water bleeding of cement-based materials modified by CNT was evaluated by Manzur *et al.* (2016). The researchers did not observe the water bleeding in cement mortar modified by CNT. However, the number of researches devoted to these issues is not enough and require further realization.

The nanoparticles and nanostructures influence on the technological properties of cement-based materials. The action mechanism of nanoparticles consists of the filling or nucleating effect and chemical interactions between nanoparticles, dispersing agent and cement. Mainly, nanoparticles decrease the flowability of cement-based materials due to their small size and high specific surface area.

1.6. The Hydration of the Cement Mixtures Modified by the Nanoparticles

Modification of cement-based materials by nano additives leads to the changes in their hydration kinetics. Despite a significant number of researches devoted to this topic, the mechanisms of influence of nanoparticles on hydration processes in cement-based materials are not clear enough and require further investigation (Senf *et al.* 2012; Xiao *et al.* 2019; Kawashima *et al.* 2013).

Senf *et al.* (2012) established the remarkable changes for samples modified separately by nano-SiO_2 and nano-TiO_2, especially on the extension of the dormant period and also on the maximum exothermic peak. Bjornstrom *et al.* (2004) & Meng *et al.* (2019) confirmed the acceleration effect of nano-SiO_2 as well. The researchers paid attention to the impact of the particle size of

nano-SiO_2 on the degree of hydration. They revealed that nano-SiO_2 of 15 nm accelerates hydration rate in an early period more effectively, promotes hydration into the diffusion reaction stage earlier and inhibit the diffusion reaction in a late period more obviously in comparison with nano-SiO_2 of 50 nm.

Addition of nano-TiO_2 to cement-based materials resulted in the acceleration effect of cement hydration processes. The modification by nano-TiO_2 in the dosage of 5% bwoc decreases the initial and final setting time of cement paste by 76.5% and 46.2%, respectively. The duration of the induction period was reduced by 35% in the case of modification by 5% nano-TiO_2 (Zhang *et al.* 2015).

In addition to nano-SiO_2 and nano-TiO_2, the modification of cement-based materials may be performed by nanoalumina, xonotlite- and tobermorite-type C-S-H-seeds. Land & Stephan (2015) established the accelerating effect of nano-SiO_2 and C-S-H-seeds on cement hydration and the retardation effect of nanoalumina. In contrast to this research, Zhou *et al.* (2019a) demonstrated the accelerating effect in the case of modification by nanoalumina. The researchers paid attention not only to the filler effect of nanoparticles but also to a chemical effect. The nanoalumina can be dissolved in pore solution. The chemical impact caused by dissolving of nano-alumina in pore solution in combination with filler effect leads to the acceleration of early-age hydration of Portland cement, speeds up the consumption of gypsum and, as a consequence, promotes the hydration of C_3A.

The effect of carbon nanomaterials, such as GNP, CNF and CNT on hydration processes in cement-based materials was studied as well. The modification by GO promotes the acceleration effect. Kjaernsmo *et al.* (2018) observed the increase of hydration heat of cement mortar modified by 0.2% bwoc of water dispersed GO. Lin *et al.* (2016) investigated the hydration of cement-based materials modified by GO. They established the catalytic behaviour of GO which explains the remarkable acceleration of the hydration rate of nanomodified cement-based materials. The researchers described the catalytic role of GO in the hydration of cement based on the oxygen-containing function groups, which create adsorption sites for water and cement with further formation of crystal nuclei for cement hydrates, and water molecules on GO, which constitute a water reservoir and water channels for hydration of cement.

However, there is the opposite point of view on the hydration of cement-based materials modified by GO. Horszczaruk *et al.* (2015) investigated the effect of 3% bwoc of GO on the cement composites and revealed that the kinetics of the hydration did not strongly alter in the case of modification by 3% bwoc of GO.

The modification of cement composites by CNF affects on hydration as well. Meng & Khayat (2018) presented that the modification by CNF extends

the duration of induction period, but increase the cumulative heat or the degree of cement hydration.

Tolmachev & Belichenko (2014) determined the prolongation of the initial and final setting time by 45 min and 75 min, respectively, in case of a modification of cement paste by carbon nanoparticles in the dosage of 0.0225% bwoc.

The effect of CNT on cement hydration processes is correlated with the impact of other types of nanomaterials. Mostly, the introduction of CNT accelerates the hydration process of cement-based materials, however there are some opposite research results.

Konsta-Gdoutos *et al.* (2017) noticed that modification by CNT had slight acceleration effect on the cement hydration. Makar & Chan (2009) noticed the acceleration effect of hydration reaction of the C_3S in ordinary Portland cement paste modified by CNT which was explained by the fact that CNT act as nucleating sites for the C_3S hydration products. Manzur *et al.* (2016) obtained that CNT influences both the initial C_3A and the C_3S hydration products and established that cement mixes with CNT require less time for setting. The decrease of setting time by 14% was observed for nanomodified cement mortar with W/C ratio of 0.60. Nadiv *et al.* (2016), Cui *et al.* (2015) & Guan *et al.* (2020), Alatawna *et al.* (2020), Li *et al.* (2019) also observed the acceleration effect of hydration reaction kinetics in the course of the researches with CNT. Guan *et al.* 2020 associated the acceleration of hydration processes in cement-based materials with MWCNT by the nucleating effect.

The opposite effect of CNT on the cement hydration kinetics is described in the researches of Isfahani *et al.* (2016), Leonavicius *et al.* (2018), Amin *et al.* (2015) & Tafesse *et al.* (2019). Isfahani *et al.* (2016) investigated the effect of pristine and functionalized CNT on the properties of cement composites. They established the deceleration of the hydration of C_3A, which is linked with a reduction of the heat produced with respect to the samples without sonication. The remarkable decrease in cumulative heat by 43.4% was established for the sample modified by 0.3% bwoc of pristine CNT. The reason for appeared deceleration effect was explained by agglomeration of CNT around the cement grains which hinders C_3A hydration. Leonavicius *et al.* (2018) identified the retardation of initial and final setting time in the case of a modification of cement paste by CNT in the dosage of 0.005–0.5% bwoc. The addition of MWCNT in the dosage of 0.5% bwoc prolonged the initial and final setting time by 130% and 110%, respectively. Amin *et al.* (2015) investigated the effect of CNT on the properties of OPC and blended cement with solid waste generated from clay bricks industry. XRD, DSC and SEM analysis performed in the course of the current research did not reveal the effect of CNT on the hydration of ordinary Portland cement and blended cement-based material. Tafesse *et al.* (2019) concluded that pure CNT have little impact on the cement hydration from a chemi-

cal standpoint and lower the hydration from a physical perspective caused by agglomeration processes of CNT.

Nano additives lead to the acceleration of hydration processes in cement-based materials. However, the opposite effects of nanomaterials are described in some researches. Thus, further investigation on the hydration of nanomodified cement-based materials is still relevant nowadays.

1.7. Conclusions of Chapter 1 and Formulation of the Objectives of the Thesis

Based on the literature review, the following conclusions can be drawn:

1. The plasticizing effect of Pl is determined by the number of factors such as changes of zeta potential, different colloidal and chemical processes on the phase boundary, adsorption processes on the surface of cement particles, properties of used cement and Pl. Cement suspension stability with Pl can be controlled by the balance of attractive and repulsive forces. The variation of molecular structures of Pl allows managing by the properties of cement-based materials in a fresh and hardened state.
2. The understanding of retardation mechanisms of Pl, managing by the amount of entraining air, water bleeding degree, flowability in cement-based materials is necessary for managing by the technological properties and performance characteristics of concrete.
3. The mechanical and chemical methods are effective tools for nanoparticles homogenization. The combination of different techniques contributes to the better nanoparticles distribution in aqueous suspension and leads to the further improvement of cement composites modified by them. The further investigation of the homogenization methods with the establishment of their optimal modes is needed.
4. The addition of nanoparticles and nanostructures into cement-based materials has a significant effect on their properties in a fresh and hardened state. The understanding of action mechanisms of nanoparticles and searching for the effective methods of homogeneous introduction into a cement matrix are required for their effective usage in cement-based materials.
5. The nanoparticles and nanostructures influence on the technological properties and hydration of cement-based materials. Mainly, the action mechanism of nanoparticles consists of the filling or nucleating effect and chemical interactions between them and cement particles. Modifi-

cation by nanoparticles decreases the flowability of cement paste and concrete mixture. Nano additives lead to the acceleration of hydration processes in cement-based materials. However, the opposite effects of nanomaterials on the hydration kinetics were observed in some researches.

The object of research is cement-based materials modified by MWCNT suspension together with plasticizing admixtures in a fresh and hardened state.

The study is dedicated to the influence of MWCNT suspension in combination with plasticizing admixtures on the rheological properties of cement-based mixtures, hydration process of cement and microstructure of hardened cement paste.

In order to achieve the aim of the thesis, the following tasks are formulated:

1. To determine the optimal homogenization method of MWCNT suspension and evaluate suspension properties after homogenization process and in time after suspension ageing.
2. To assess changes in rheological parameters (yield stress, plastic viscosity, shear thickening/ thinning indexes) of cement pastes modified by MWCNT suspension with and without plasticizing admixtures.
3. To evaluate the impact of MWCNT suspension on the stability of cement pastes with and without plasticizing admixtures.
4. To study the changes in the hydration processes, microstructure and morphology of cement-based materials modified by MWCNT suspension.

2

Materials and Testing Methods of Nanomodified Cement Composites

This chapter experimentally investigates the effect of MWCNT suspension with and without plasticizing admixtures on the properties of cement-based materials in a fresh and hardened state. It describes the applied materials, methods of homogenization of MWCNT suspensions and their characterization, methods of rheological testing of nanomodified cement pastes. Chapter 2 also includes the information about the methods used for testing of hydration processes and performance of cement-based materials modified by MWCNT. This chapter contains the material presented in journal publication Skripkiunas *et al.* (2017), Skripkiunas *et al.* (2018), Skripkiunas *et al.* (2019), Karpova et al. (2019) and conference proceedings Skripkiunas *et al.* (2018a), Skripkiunas *et al.* (2018b), Skripkiunas *et al.* (2019).

2.1. Materials Used in the Research

2.1.1. The Characteristics of the Portland Cement

The Portland cement without mineral additives CEM I 42.5 R conforming to EN 197-1 was used. The mineral and chemical composition of the cement is presented in Table 2.1.

Table 2.1. Mineral and chemical composition of the cement

Component	Amount, %	Component	Amount, %
Tricalcium silicate (C_3S)	57.9	CaO	63.56
Dicalcium silicate (C_2S)	15.6	MgO	3.13
Tricalcium aluminate (C_3A)	7.5	SO_3	0.78
Tetracalciumaluminoferrite (C_4AF)	11.9	K_2O	1.15
Al_2O_3	5.23	Na_2O	0.10
Fe_2O_3	3.44	Cl^-	0.007
SiO_2	20.63	CaO_{free}	1.4

The ordinary Portland cement with the content of tricalcium silicate less than 60%, dicalcium silicate about 15% and tricalcium aluminate up to 8% was taken in the current research as more widely used Portland cement in construction practice.

Table 2.2. Physical and mechanical properties of cement

Property	Value	Property	Value
2-day compressive strength, MPa	28±2	Volume stability, mm	1.0
28-day compressive strength, MPa	55±3	Water consumption, %	26.6
Initial setting time, min	180	Residue on the 90 μm sieve, %	1.5
Final setting time, min	225	Specific surface (cm^2/g)	3552

The physical and mechanical properties of applied cement are listed in Table 2.2. The specific surface area determined by the Blaine method according to EN 196-6 was of 3552 cm^2/g. The compressive strength of used cement at 28 days reached the value of about 55 MPa.

The known data about cement from the producer is essential for the prediction of properties of cement systems in the fresh and hardened state. The parameters of cement are one of the decisive factors which determine the

rheological behaviour of cement paste, the compatibility of cement with chemical admixtures and have a further impact on the properties of cement-based materials in the hardened state.

2.1.2. The Characteristics of the Plasticizing Admixtures

The LS, NF and PCE plasticizers were applied in the research as a dispersant to distribute the nanotubes in the volume of water suspension and as a plasticizing admixture for the cement-based materials.

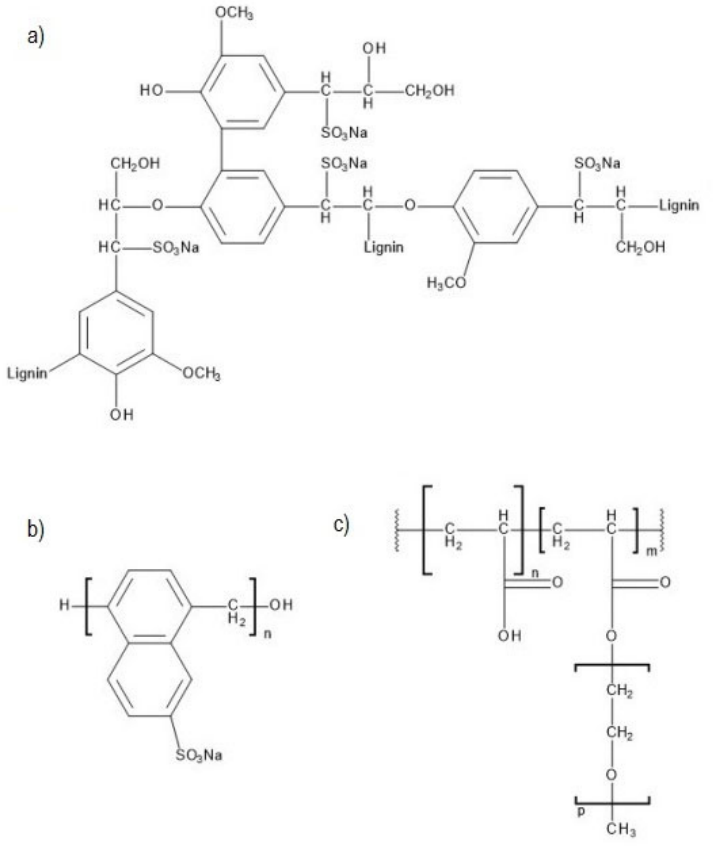


Fig. 2.1. Chemical structure of plasticizers: a) lignosulphonate;
b) sulfonated naphthalene formaldehyde condensate and
c) polycarboxylate ether (Aitcin & Flatt 2016a)

Table 2.3. Properties of plasticizing admixtures

Characteristic	LS	NF	PCE
Form	liquid	liquid	liquid
Colour	dark brown	yellow	yellow
Dry content, %	30–40	40–50	50
Specific gravity, g/ml	1.14	1.20	1.10
pH	4.3	9.1	4.9
Electrical conductivity, mS/cm	1.93	3.59	0.91
Recommended dosage, %	0.4–1.2	0.5–2.0	0.2–2.0

The plasticizing admixtures applied in the current research are based on such polymers as lignosulphonate, sulfonated naphthalene formaldehyde condensate and polycarboxylate ether. The chemical structures of applied Pl are presented in Fig. 2.1.

The pH value as one of the crucial parameters which determine the plasticizing efficiency of Pl presents the acid behaviour for LS and PCE whereas NF possesses by the alkaline medium. The main properties of used Pl are presented in Table 2.3.

2.1.3. The Characteristics of the Multi-Walled Carbon Nanotubes Suspension

The MWCNT suspension was prepared from the pellets "Graphistrength CW 2-45" produced by the company "Arkema" (France). The pellets contain 45 wt% of MWCNT and 55 wt% of carboxymethyl cellulose (CMC). The MWCNT properties are listed in Table 2.4.

Table 2.4. Properties of multi-walled carbon nanotubes

Parameter of MWCNT	Typical value
Filament length, nm	100–10000 (0.1–10 μm)
Diameter, nm	15–20

Distilled water was used as a dispersion medium for MWCNT homogenization. The SEM image of MWCNT bundles obtained by MIRA3 TESCAN is shown in Fig. 2.2.

CMC included into pellets "Graphistrength CW 2-45" is applied as a dispersing agent for homogeneous distribution of nanotubes in the volume of the

aqueous suspension. The presence of carboxyl groups in the chemical structure of CMC (see Fig. 2.3) explains its dispersing efficiency in the course of the suspension homogenization.

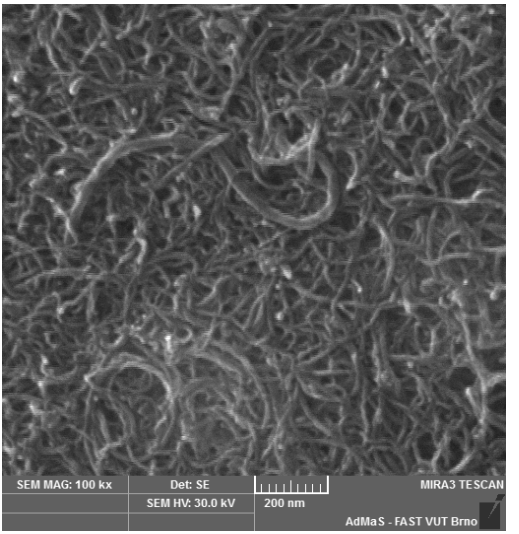


Fig. 2.2. Scanning electron microscopy of multi-walled carbon nanotubes bundles obtained by MIRA3 TESCAN

For the investigation of the separate impact of CMC on the cement pastes, CMC produced by the company "Arkema" (France) was applied.

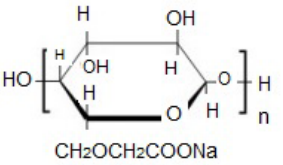


Fig. 2.3. Chemical structure of carboxymethyl cellulose (Aitcin & Flatt 2016a)

The homogenization of MWCNT in the medium of CMC requires paying attention to chemical interactions between CMC and functional groups of applied Pl in the cement systems, which can have an impact on the properties of the cement-based materials in the fresh and hardened state.

2.2. The Preparation of Suspension and Nanomodified Cement Compositions

2.2.1. The Preparation of Suspension

The MWCNT suspension was prepared in the following way. The pellets "Graphistrength CW 2–45" were immersed in hot water with a temperature of 75 °C and stirred by a standard mixer agitation of 1000 rpm during 5 min. The volume of the homogenizing suspension was of 200 ml.

After that, MWCNT suspension was subjected to ultrasonication for duration of 3, 6, 9, 12 min. The ultrasonication was performed by Bandelin Sonopuls HD 3400 ultrasonic homogenizer (400 W, 20 kHz) with probe VS 200 T (Ø25 mm, amplitude – 82 μm).

The ultrasonication technique was compared with a method based on the rotor-stator principle. Rotor-stator homogenization was performed by Ultra-Turrax Dispersers T25 digital with frequency 50/60 Hz at speed 5000 rpm for a duration 6 and 30 min. The scheme of the homogenization process is presented in Fig. 2.4. The image of ultrasonication and rotor-stator equipment is presented in Fig. 2.5 a, b.

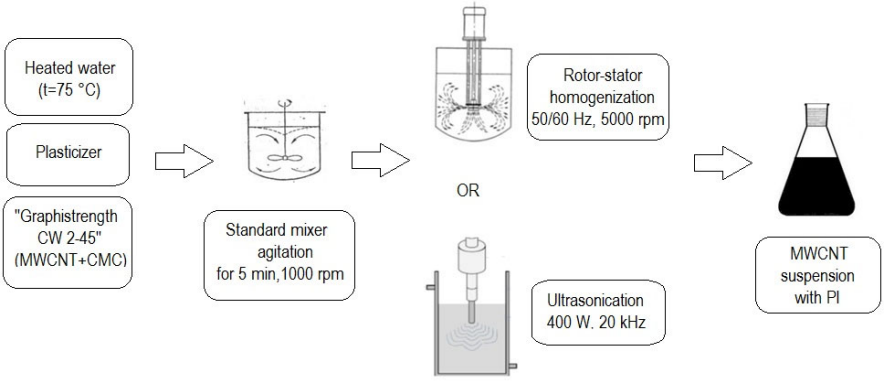


Fig. 2.4. Scheme of homogenization of multi-walled carbon nanotubes suspension

The compositions of MWCNT suspensions prepared for the comparison between ultrasonication and rotor-stator method are listed in Table 2.5. The ratio

between MWCNT and Pl, their dosages and time of homogenization were chosen based on the literature sources (Leibscher *et al.* 2017; Sobolkina *et al.* 2012).

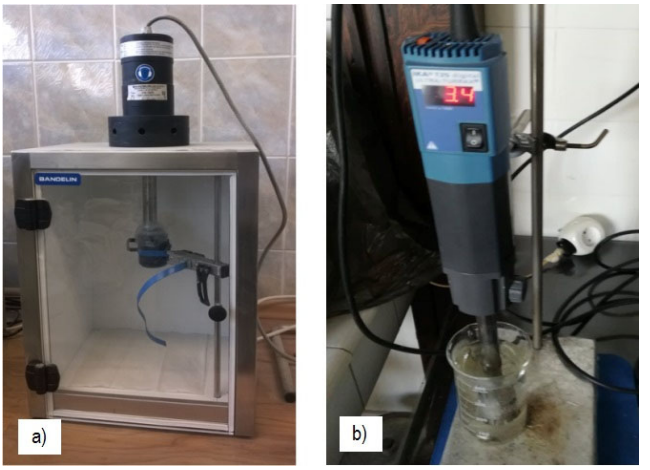


Fig. 2.5. Equipment for suspension homogenization: a) ultrasonication and b) rotor-stator homogenizer

Table 2.5. Composition of multi-walled carbon nanotubes suspensions for ultrasonication and rotor-stator homogenization

Designation	MWCNT* in volume of suspension, %	CMC* in the volume of suspension, %	PCE in volume of suspension, %	Ratio between MWCNT and PCE	Time of ultrasonication /rotor-stator homogenization, min
Ultrasonication					
S0	0.28	0.34	1.12	1:4	0
S3	0.28	0.34	1.12	1:4	3
S6	0.28	0.34	1.12	1:4	6
S9	0.28	0.34	1.12	1:4	9
S12	0.28	0.34	1.12	1:4	12
Rotor-stator homogenization					
ST6	0.28	0.34	1.12	1:4	6
ST30	0.28	0.34	1.12	1:4	30

* MWCNT suspension was prepared based on pellets “Graphistrength CW 2-45”consisted of MWCNT and CMC (see section 2.1.3)

Table 2.6. Composition of multi-walled carbon nanotubes suspensions with and without plasticizing admixture homogenized by ultrasonication method

Designation	MWCNT suspension without Pl		Designation	MWCNT suspension with Pl			Time of ultrasonication, min
	MWCNT in volume of suspension, %	CMC in the volume of suspension, %		MWCNT in volume of suspension, %	CMC in the volume of suspension, %	Pl in volume of suspension, %	
S15	0.015	0.018	SP15	0.015	0.018	3.8	6
S30	0.030	0.037	SP30	0.030	0.037		
S60	0.060	0.073	SP60	0.060	0.073		
S120	0.120	0.146	SP120	0.120	0.146		
S240	0.240	0.293	SP240	0.240	0.293		
S480	0.480	0.586	SP480	0.480	0.586		
S960	0.960	1.171	SP960	0.960	1.171		

The ultrasonication for 6 min was chosen as an optimal homogenization method in the course of the research. The further homogenization of MWCNT suspensions was performed by ultrasonication technique for 6 min. 4 types of MWCNT suspensions with various MWCNT dosage were homogenized, such as MWCNT suspensions without Pl, with LS, NF and PCE plasticizers. MWCNT dosage was changed from 0 to 0.96% in the aqueous suspension. Dosage of Pl was of 3.8% (1% bwoc) in all MWCNT suspensions. The ratio between Pl and MWCNT varied from 4 to 256. The mix design of MWCNT suspension with and without Pl homogenized by ultrasonication method is presented in Table 2.6.

2.2.2. The Preparation of the Cement Pastes with Suspension and Plasticizers

The cement pastes were modified by MWCNT suspension prepared according to the methods described in section 2.2.1.

200 g of cement was used for preparing of cement paste for each rheological test. The MWCNT suspension was used as mixing water for the cement paste modification. The dosage of MWCNT varied from 0 to 0.24% bwoc. The dosage

of LS, NF and PCE plasticizers was of 1% bwoc for all cement pastes modified by MWCNT suspension in combination with Pl. The mix design of the cement pastes for the rheological test is presented in Table 2.7, 2.8. The water to cement ratio (W/C) of the cement pastes during the rheological test was equal to 0.30 for cement pastes without Pl and 0.25 for cement paste with Pl.

Table 2.7. Mix design of the cement pastes for rheological test (without plasticizing admixture)

Desig-nation	Cement, g	W/C	Water, g	MWCNT suspen-sion, g	MWCNT, % bwoc	CMC, % bwoc
C0	200	0.30	60	0	0	0
C4			0	60	0.00375	0.00460
C8					0.0075	0.0092
C15					0.015	0.018
C30					0.030	0.037
C60					0.060	0.073
C120					0.120	0.146
C240					0.240	0.293

Table 2.8. Mix design of the cement pastes for rheological test (with plasticizing admixture)

Desig-nation	Cement,g	W/C	Water, g	Pl , % bwoc	MWCNT suspen-sion with Pl, g	MWCNT, % bwoc	CMC, % bwoc
CP0	200	0.25	50	1	0	0	0
CP4			0		50	0.00375	0.0046
CP8						0.0075	0.0092
CP15						0.015	0.018
CP30						0.030	0.037
CP60						0.060	0.073
CP120						0.120	0.146
CP240						0.240	0.293

The scheme of cement paste modification by MWCNT suspension with and without Pl is represented in Fig. 2.6.

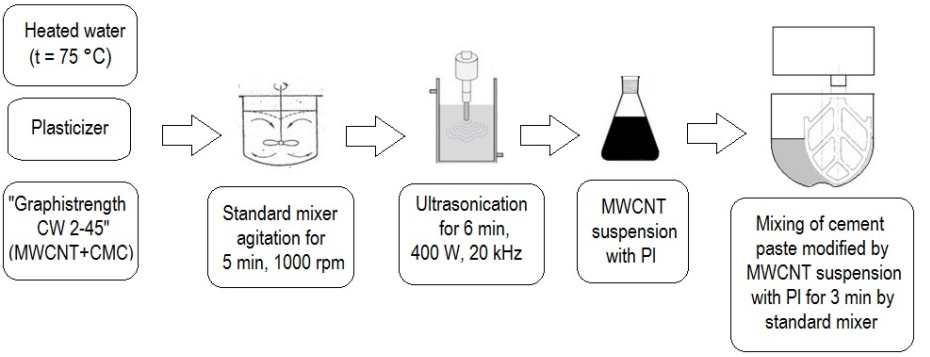


Fig. 2.6. Modification of cement paste by multi-walled carbon nanotubes suspension with plasticizing admixture

The setting time test of cement pastes modified by MWCNT suspension was carried out according to EN 480-2 at W/C ratio of 0.30. MWCNT dosage in the setting time test was of 0.06% bwoc.

Table 2.9. Mix design of the samples for calorimetry testing

Designation	Cement, g	W/C	Water, g	Pl, % bwoc	MWCNT, % bwoc	CMC, % bwoc
Cement pastes without Pl						
H0	3	0.50	1.5	0	0	0
HC4	3	0.50	1.5	0	0	0.04
HC7	3	0.50	1.5	0	0	0.07
HC14	3	0.50	1.5	0	0	0.14
H3	3	0.50	1.5	0	0.03	0.04
H6	3	0.50	1.5	0	0.06	0.07
H12	3	0.50	1.5	0	0.12	0.14
Cement pastes with Pl (LS, NF, PCE)						
HP0	3	0.50	1.5	1	0	0
HP3	3	0.50	1.5	1	0.03	0.04
HP6	3	0.50	1.5	1	0.06	0.07
HP12	3	0.50	1.5	1	0.12	0.14

Taking into account the presence of CMC in MWCNT suspension (as a dispersing agent), the setting time test of cement paste separately modified by CMC in the dosage of 0.07% bwoc was provided.

The mix design of the samples for the calorimetry investigation is shown in Table 2.9. The samples for the calorimetry testing were prepared in the following way. 3 g of cement was weighted in a special glass ampule. W/C ratio was of 0.50 for all samples. The dosage of MWCNT was taken in the range from 0 to 0.12% bwoc. The Pl added in the dosage of 1% bwoc for all testing samples. The ampoules with cement were supplemented with syringes containing the mixing water, Pl and MWCNT suspension. The calorimetry test of the samples modified by CMC (dispersing agent of MWCNT suspension) in the appropriate dosage was performed to evaluate the separate MWCNT impact on the cement hydration.

2.3. The Characteristics of the Research Methods

The present section describes the methods of MWCNT suspension homogenization and characterization, methods of testing of nanomodified cement-based materials in a fresh and hardened state.

2.3.1. The Study of Suspension Properties

The MWCNT suspensions after homogenization were characterized by pH, electrical conductivity, zeta potential, particle size and surface tension measurements. The properties of the MWCNT suspension were tested after one month to evaluate their stability during the ageing process.

pH test was performed by pH-meter Mettler-Toledo EL 20 with limits of error ± 0.01 pH. The electrode with a gel electrolyte was used.

Electrical conductivity was measured by Mettler-Toledo EL30. The measurement range of it is 0.1 to 199.1 mS/cm, limits of error ±0.5%. The electrode for medium to high conductivities (10 μS/cm …500 mS/cm) was applied.

Particle size analysis and zeta potential measurements of MWCNT suspension were performed by particle size and zeta potential analyser Delsa Nano C, Beckman Coulter.

Particle size analysis was based on the principle of photon correlation spectroscopy (Fig. 2.7) with a resolution of measurements placed from 0.6 nm to 7 μm.

Zeta potential measurements were based on the electrophoretic light scatter-

ing principle (Fig. 2.8) with a range of measurement from –150 mV to +150 mV.

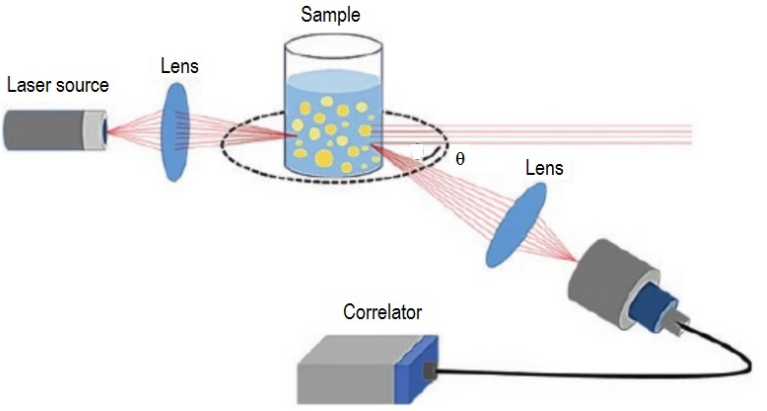


Fig. 2.7. Principle of photon correlation spectroscopy (Choudhary et al. 2019)

The polydispersity index (PDI), which is the dimensionless measure of the broadness of the size distribution, was evaluated for the MWCNT suspension with and without Pl. PDI was calculated automatically as a ratio between the square of standard deviation and the square of mean diameter by the software of analyser Delsa Nano C, Beckman Coulter. The value of PDI is ranged between 0 and 1. The value closer to 0 and no more than 0.3 confirms the better homogeneity of particles.

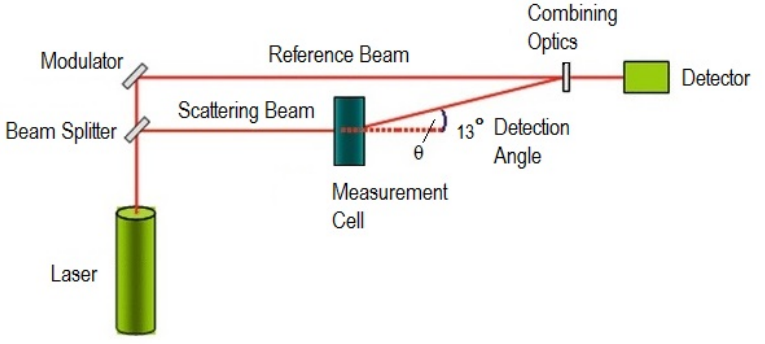


Fig. 2.8. Electrophoretic light scattering principle (McNeil-Watson 2013)

The surface tension of MWCNT suspension with and without Pl was measured based on the stalagmometric method by stalagmometer Traube (Fig. 2.9.) with a measurement accuracy of 1 mN/m.

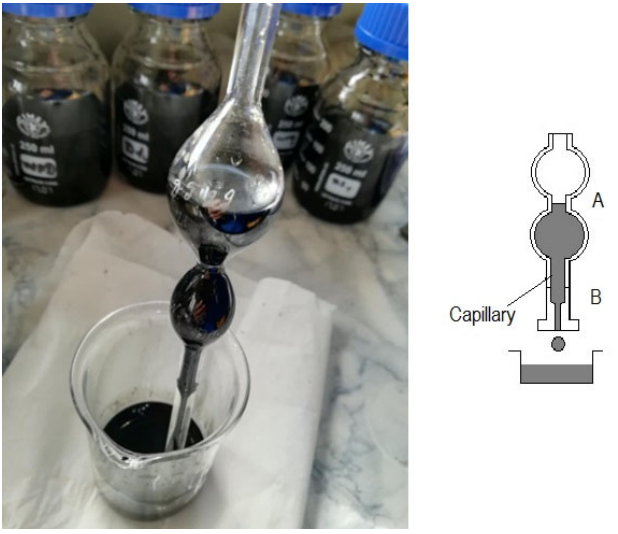


Fig. 2.9. Stalagmometer Traube

The stalagmometric method consists of the determination of drops number which is formed in the course the flowing of liquid from a capillary tube of known volume.

The surface tension of the studied liquid is calculated based on the formula:

$$\sigma_x = \sigma \cdot \frac{N}{N_x} \cdot \frac{d_x}{d}, \tag{2.1}$$

where σ is the surface tension, mN/m; N is the number of drops; d is the density, g/cm^3 of distilled water (liquid with known parameters); σ_x, N_x, d_x are the same for studied liquid (Wilson *et al.* 1968).

Fourier transform infrared (FTIR) spectroscopy was undertaken to identify the chemical bondings between CMC (dispersing agent in MWCNT suspension) and functional groups of Pl (PCE plasticizer) in MWCNT suspension. FTIR was provided by the equipment described in section 2.3.4.

2.3.2. The Study of Rheological Properties and Water Bleeding of Cement Pastes

The rheological test was carried out by rotational rheometer Rheotest RN 4.1 with coaxial cylinders. The scheme of the cylinder measuring system of rotational rheometer Rheotest RN 4.1 with coaxial cylinders is shown in Fig. 2.10.

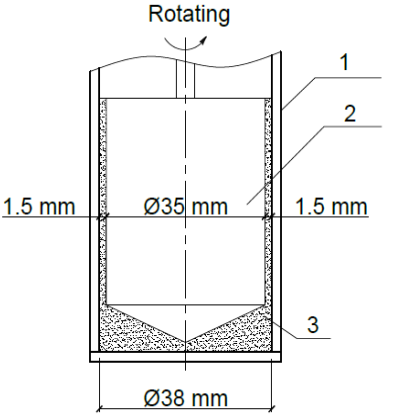


Fig. 2.10. Scheme of the cylinder measuring system of rotational rheometer Rheotest RN 4.1 with coaxial cylinders: 1 – assembled measuring cup, 2 – rotating cylinder rotor, 3 – cement paste

The assembled measuring cup (1) with coupling is poured by cement paste (3) and fixed in the equipment stand. The rotating cylinder rotor (2) is placed inside the measuring cup (1) with a gap between them about 1.5 mm and rotates during the test. The intrinsic friction of cement paste layers takes place between measuring cup (1) and cylinder rotor (2). The testing data are written when the rotating cylinder rotor makes a turn due to its connection with measuring scale. The rheological test was provided according to the mode presented in Fig. 2.11 at 5, 60, 120 min after cement paste mixing.

The rheological properties of cement pastes modified by MWCNT suspension without Pl were compared with the reference sample without admixtures. The cement paste with Pl was taken as a reference sample in the case of studying of cement pastes modified by MWCNT suspensions with Pl.

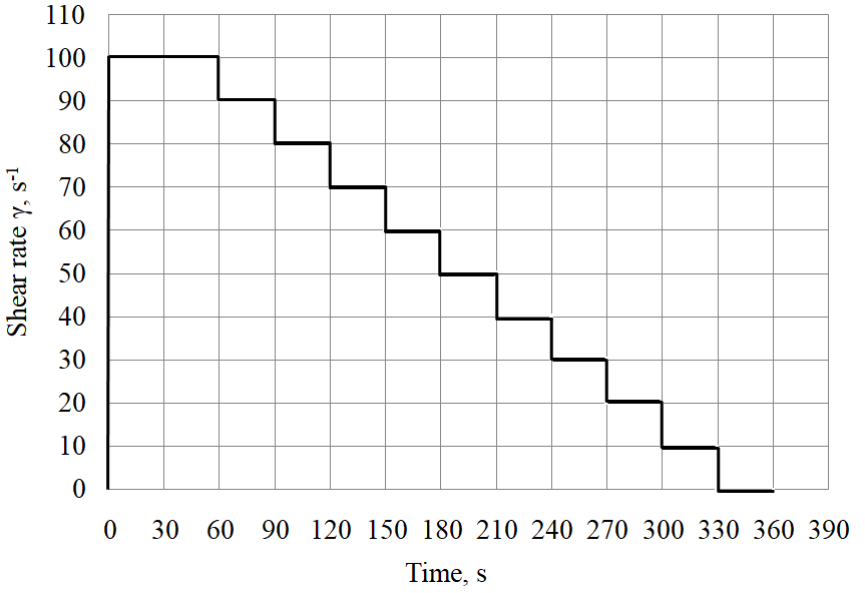


Fig. 2.11. Shear rate mode of the rheological test during the time

The main rheological parameters, such as yield stress (τ_0) and plastic viscosity (μ) were determined in the course of approximation of flow curve (dependence between shear stress (τ) and shear rate (γ) in the range from 0.1 to 100 s^{-1} based on Herschel-Bulkley model. The Herschel-Bulkley model is more widely used model for the description of the flow behaviour of cement-based materials with shear thinning or shear thickening flow behaviour, which is expressed by the Equation:

$$\tau = \tau_0 + \mu \cdot \dot{\gamma}^n, \tag{2.2}$$

where τ is shear stress, Pa; τ_0 is yield stress of the cement paste, Pa; μ is plastic viscosity, Pa·s; $\dot{\gamma}$ is shear rate, s^{-1}; n is shear thinning or shear thickening index if $n < 1$ or $n > 1$, respectively (Aitcin & Flatt 2016c).

The approximation of experimental points, according to the Hershel-Bulkley model, is presented in Fig. 2.12.

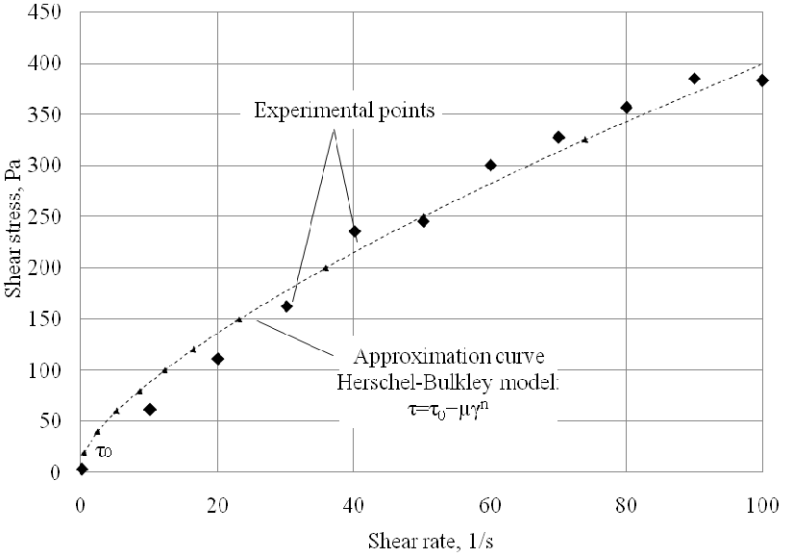


Fig. 2.12. Approximation of experimental flow curve by Herschel-Bulkley model

Amount of bleeding water was determined according to the following method. 50 g of MWCNT suspension prepared by ultrasonication method with and without Pl was poured into 200 ml plastic container. 50 g of cement was added to to the plastic container in 1 min. Subsequently, MWCNT suspension and cement were mixed continuously for 4 min in the plastic container. The plastic container was remained to stand without moving and shaking during the test. The bleeding water was collected from the surface of sedimented cement by the syringe after 2 hours since the reference point.

Water bleeding was calculated according to the Equation:

$$K_b = \frac{a-b}{a} \cdot 100\%, \tag{2.3}$$

where K_b is the coefficient of water bleeding, %; a is the initial volume of cement paste, cm^3; b is the volume of sedimented cement, cm^3.

In addition to the water bleeding test of the cement pastes modified by MWCNT suspension homogenized together with Pl by ultrasonication method, water bleeding test was undertaken for MWCNT suspension and Pl which were not subjected to joint ultrasonication treatment. The dosage of MWCNT varied from 0 to 0.24% bwoc, Pl was of 1% bwoc. In this case, MWCNT suspension and Pl were added to mixing water and mixed together manually for 1 min be-

fore addition to the cement-based materials. The further water bleeding test was carried out according to the method described above for MWCNT suspension with Pl homogenized together by ultrasonication.

2.3.3. The Calorimetric Investigation and Setting Time of Cement-Based Material

The calorimetry investigation was performed by isothermal calorimeter TAM AIR III with measurements range of ±600 mW. TAM AIR is an eight-channel, isothermal, heat conduction calorimeter operating in the multi-watt range. A calorimeter block is formed by eight calorimetric channels and housed in a temperature-controlled air thermostat. The calorimetric channels are constructed in twin configuration with one side for the sample and the other side for a reference. In the course of an experiment, the studied sample is compared directly with the heat flow from the inert reference. The voltage differences are a quantitative expression of the overall rate of heat production in the sample. The measuring principle based on usage of twin configuration enhances the heat flow stability and reduces noise within the system.

In the course of the present research, the cement hydration investigation was performed in the following way. Firstly, the setting of operating temperature, calibration of the instrument, preliminary checks were provided. Then studied and reference samples were prepared. 3 g of cement in solid state and distilled water, used as a reference, were held in 20 mL glass ampoules. The ampoules with cement were supplemented with syringes containing the mixing water, Pl and MWCNT suspension. After preparation of samples, the experiment was started. The loading of studied and reference samples into calorimetric channels and injection of mixing water from the syringes into ampoules with anhydrous cement was performed according to the instructions of instruments software. The calorimetry investigation of cement-based materials with different types of Pl and MWCNT suspension was carried out within two days.

The setting time test of cement pastes modified by MWCNT suspension was carried out according to EN 480-2 by standard Vicat apparatus at the temperature of 20±2 °C during the test.

2.3.4. The Investigation of Mineral Composition and Microstructure of Nanomodified Cement Composites

The SEM, X-Ray and thermal analysis were undertaken to investigate the MWCNT distribution in the cement matrix and evaluate its effect on the mor-

phology of cement hydration products. The identification of chemical bondings in the nanomodified cement-based materials was provided by FTIR spectroscopy.

The microstructure of the materials was explored upon the use of scanning electron microscopy (SEM) equipment MIRA 3 Tescan. The parameters of electron microscopy were the following: voltage 30 kV, distance to the surface of the specimen – from 7 to 10 mm. The peculiarities of the microstructure were identified in examining the split surface of the specimens. The image was formed on registering the signal of secondary electrons. Before the test, the cleavage surface was covered with a thin golden layer upon applying the method of gold electron vacuum evaporation. SEM was used to observe the MWCNT suspension and nanomodified hardened cement pastes.

The X-ray diffraction (XRD) analysis of the phase composition of materials was carried out upon applying diffractometer DRON-7. To obtain X-ray radiation Cu Kα spectrum ($\lambda = 0.1541837$ nm), a graphite monochromator was used. The parameters of the tests were following: voltage – 30 kV; current – 12 mA; the range of the diffraction angle – from 4 to 80°, the detector movement step – 0.02°; the duration of the intensity measuring in the step – 0.5 s.

To perform the quantitative analysis of data obtained by XRD, the Rietveld phase analysis was carried out. The quantitative Rietveld phase analysis of the cement samples was performed using a graphics based profile analysis program ("TOPAS") and structure data taken from PDF4 database.

The simultaneous thermal analysis (STA) was employed for the measuring phase transformation of the products at a heating rate of 10 °C/min, the temperature ranged from 30 to 1000 °C in the nitrogen atmosphere, the mass of the sample was 15 mg. The test was carried out on a Linseis STA PT-1000 (Germany) instrument. The ceramic sample handlers and crucibles of Pt/10 wt% Rh were used.

FTIR spectra of hardened cement paste modified by PCE and MWCNT suspension and PCE at the age of 7 days were recorded by using a SPECTRUM GX 2000 spectrophotometer. The data were recorded in the spectral range from 400 to 4000 cm^{-1}.

Porosity testing of nanomodified cement composites was performed by nitrogen adsorption–desorption porosimetry. The experiment was carried out for the hardened cement paste modified by MWCNT in the dosage from 0 to 0.12% bwoc after 7 days of curing at standard conditions. The cement samples were dried at the oven at the temperature of 60 °C during 14 days before porosity testing. The textural parameters of the samples were determined by nitrogen adsorption–desorption isotherms at −196 °C (77 K) using a Quantachrome Autosorb-iQ-KR/MP automated gas sorption analyzer. Prior to the analysis, the powder samples were outgassed under vacuum at 85 ºC for 2h. The specific surface

area was calculated using the BET (Brunauer-Emmett-Teller) equation. The pore ize distribution was determined by applying the density functional theory (DFT). The total pore volume was measured from adsorption isotherm by the uptake of nitrogen at a relative pressure of $P/P_0 = 0.99$. All calculations were performed using ASiQwin (Version 2.0) program developed by Quantachrome Instrument.

2.4. Conclusions of Chapter 2

1. The efficiency of complex admixture based on MWCNT and Pl for concrete modification requires the homogeneous distribution of nanoparticles in aqueous suspension. The methods of ultrasonication and rotor-stator homogenization are effective for the preparation of the high-quality suspension and can be applied in the research.
2. The methods such as pH, electrical conductivity, surface tension, zeta potential, and particle size measurements, FTIR spectroscopy are suggested in the current research as an effective tool to analyze the properties of MWCNT suspension after homogenization.
3. As a dispersion system, suspension of nanotubes is tended to coagulation processes during the ageing period that makes it is necessary to check the properties of the suspension at least during 1 month after homogenization.
4. For the evaluation of rheological parameters of cement paste modified by MWCNT suspension with and without Pl, such as yield stress, plastic viscosity and shear thinning (thickening) indexes, rotational rheometer with coaxial cylinders is suitable. The Herschel-Bulkley model is chosen for the approximation of experimental rheological results with high accuracy for studied cement pastes.
5. The method of evaluation of water bleeding in cement pastes by means of measurements of bleeded water volume in percent from the total volume of cement paste is proposed and can be used for calculation of the coefficient of water bleeding with making a conclusion about the stability of cement paste.
6. The results of isothermal calorimetry characterise the hydration process of cement-based materials modified by MWCNT suspension with and without Pl. SEM, XRD, STA, FTIR, nitrogen adsorption-desorption porosimetry identify changes in the microstructure, mineral composition, morphology of cement hydration products and microporosity of nanomodified hardened cement pastes.

3

Structure and Properties of Cement- Based Materials with Multi-Walled Carbon Nanotubes Suspension and Plasticizers

This chapter presents the experimental results of homogenization of MWCNT suspension, its characterization and influence on the properties of cement pastes and hardened cement composites. The optimal homogenization method and optimal dosages of MWCNT were established. The rheological properties of cement pastes with MWCNT suspension and plasticizing admixtures were identified according to Herschel-Burkley rheological model. The effect of MWCNT suspension on the cement hydration and the properties of cement-based materials in a hardened state were investigated. This chapter includes the material presented in journal publication Skripkiunas *et al.* (2017), Skripkiunas *et al.* (2018), Skripkiunas *et al.* (2019), Karpova *et al.* (2019) and conference proceedings Skripkiunas *et al.* (2018a), Skripkiunas *et al.* (2018b).

3.1. Suspension Characterization

The first technological stage in the modification of cement matrix by MWCNT is a preparation of stable MWCNT suspension. The different parameters such as particle size, zeta potential, surface tension, pH and electrical conductivity are used for characterization of MWCNT suspension. The observation of MWCNT suspension during one month of ageing was performed. This section is devoted to the description of MWCNT suspension properties prepared with different MWCNT dosages, Pl, and homogenized by various methods.

3.1.1. Particle Size Analysis and Polydispersity Index

The results of particle size analysis of MWCNT suspensions subjected to ultrasonication and rotor-stator homogenization are presented in Fig. 3.1. The standard mixer agitation during 5 min is not enough to distribute the particles with nanometer size and elongated shape. In this case, the average particle size of MWCNT suspension (size of MWCNT agglomerates) reached the value about 870 nm as it is presented in Fig. 3.1.

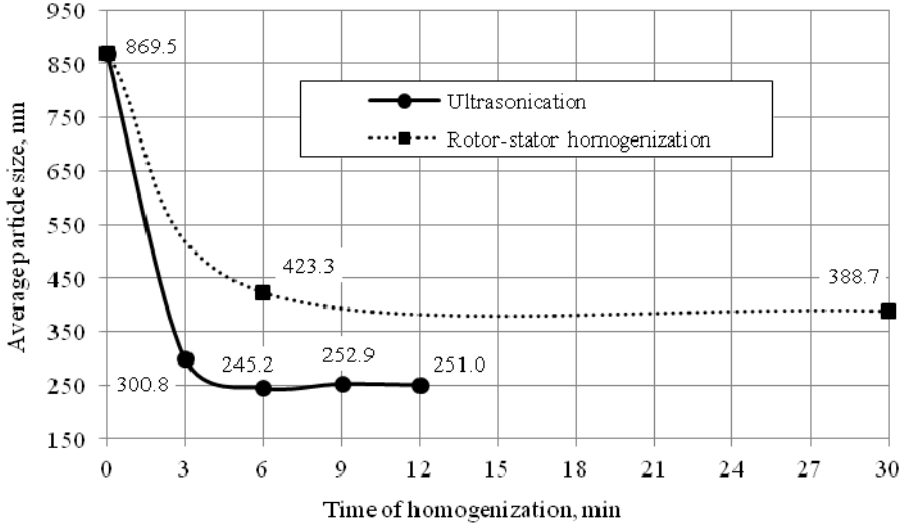


Fig. 3.1. Particle size analysis of suspension subjected to ultrasonication and rotor-stator homogenization

Ultrasonication for 3 min demonstrated the decrease in average particle size from 870 to 300 nm, which is evidence of ultrasonication effectiveness. Ultrasonication for 6 min enables to get the average particle size of 245 nm. The further increase in ultrasonication time did not reveal the significant changes in particle size distribution. The usage of rotor-stator homogenization method for 30 min led to the decrease in the average particle size from 870 nm to 388 nm. Therefore, the ultrasonication for 6 min was established as optimal homogenization method in the course of the present research.

The difference in average diameters of particles obtained by different methods may be caused by the difference in principles of homogenization, which were described above in chapter 2. The changes of PDI, which presents the dimensionless measure of the broadness of the size distribution, are shown in Fig. 3.2.

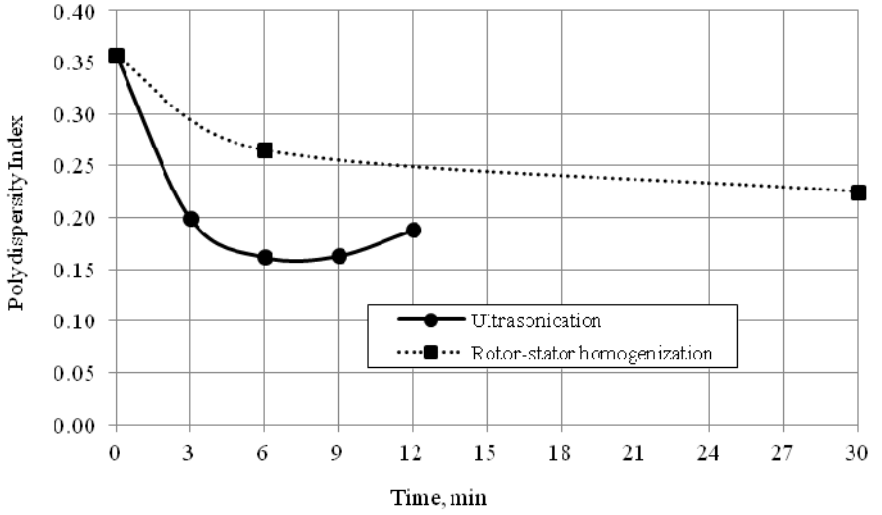


Fig. 3.2. Polydispersity index for suspension homogenized by rotor-stator and ultrasonication methods

The value of PDI closer to 0 confirms the better homogeneity of nanoparticles in water suspension. The MWCNT suspension after 6 min of ultrasonication had a smaller average particle size and PDI of 0.15, which confirms the homogeneous distribution. The ultrasonication for 6 min was used for the further investigation of MWCNT suspension with different types of Pl.

The particle size analysis revealed the different effect of Pl on the average particle size. As it is seen in Fig. 3.3, LS and NF slightly decrease the average

particles size in the suspension in comparison with MWCNT suspension without Pl and with PCE.

The minimum diameters about 220 nm and 240 nm were observed for MWCNT suspension with LS and NF, respectively. In opposite to the effect of LS and NF, the average particle size in MWCNT suspension with PCE is higher due to its chemical structure and zeta potential which is less, than it is for MWCNT suspension with LS and NF. The increase in the average particle size up to 470 nm was obtained in MWCNT suspension with PCE.

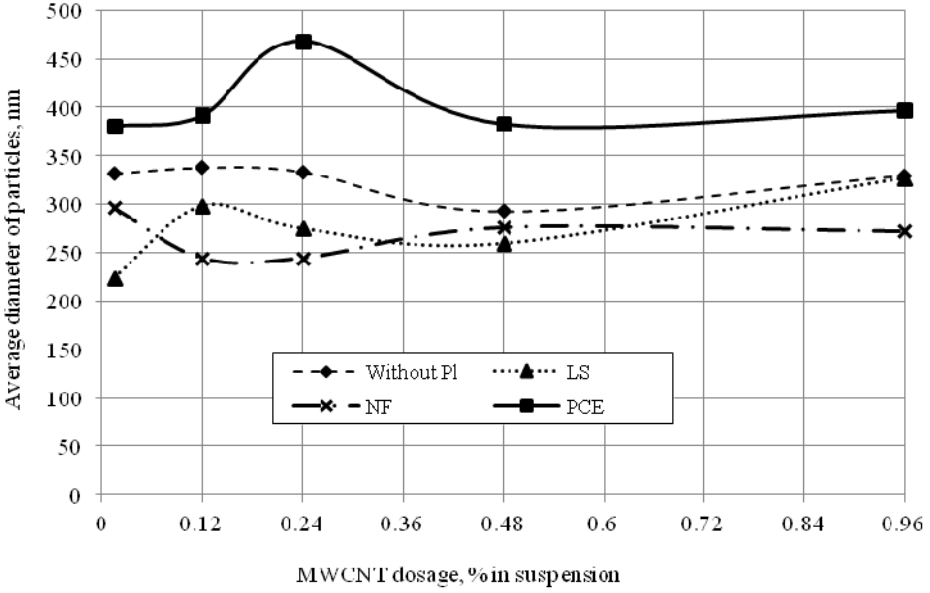


Fig. 3.3. Particle size analysis of suspension with different plasticizing admixtures and multi-walled carbon nanotubes dosage

The carboxyl groups of PCE plasticizer can be involved in the formation of intramolecular and intermolecular hydrogen bonds. Intermolecular hydrogen bonds result in the aggregation of molecules. LS and NF do not cause the aggregation of particles caused by the absence of carboxyl groups in their molecular structure. Therefore, LS and NF act as an effective dispersing agent for MWCNT suspension without a significant increase in average particles size (see section 3.1.5).

PDI was evaluated for the MWCNT suspension with and without Pl. The PDI values are presented in Fig. 3.4. Based on the results shown in Fig. 3.4, the PDI reached the minimum values for all MWCNT suspensions, but in different MWCNT dosage and with different Pl.

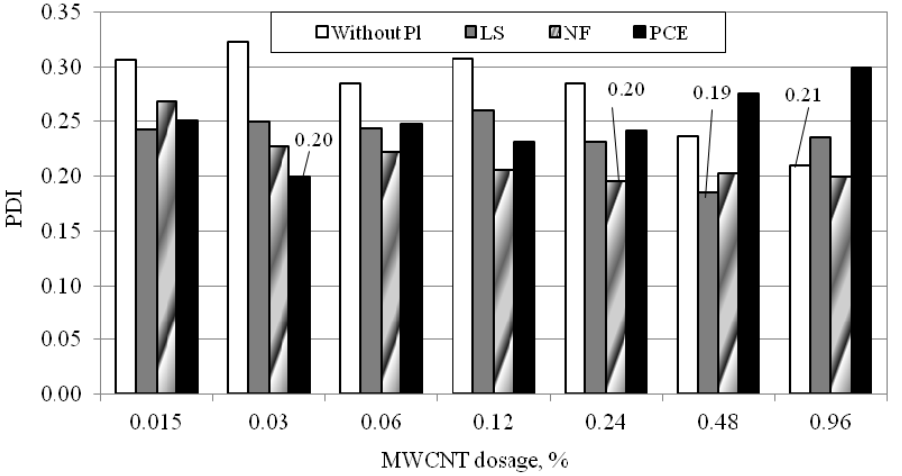


Fig. 3.4. Polydispersity index of suspension with and without plasticizing admixture

According to particle size analysis, the ultrasonication method for 6 min was chosen as optimal homogenization method for MWCNT suspension preparation in comparison with the rotor-stator technique. Various types of Pl have a different impact on MWCNT suspension characteristics. LS and NF slightly decrease the average particles size of suspension. The average particles size was about 220 nm and 240 nm, respectively, in comparison with MWCNT suspension without Pl with an average particles size about 290 nm. The average particles size was about 470 nm in case of addition of PCE to MWCNT suspension.

3.1.2. Zeta Potential and Surface Tension

Zeta potential of MWCNT suspension was determined to evaluate its stability. Also, the value of zeta potential is one of the parameters which define the plasticizing efficiency of admixtures in cement pastes. Zeta potential was evaluated for MWCNT suspensions with and without Pl. The second parameter which can explain the plasticizing effect of admixtures in cement-based materials is surface tension. Surface tension measurements of MWCNT suspension with and without Pl were performed.

First of all, the zeta potential and surface tension were evaluated for MWCNT suspension homogenized in different ultrasonication time. The results of zeta potential and surface tension measurements of MWCNT suspension homogenized for 3, 6, 9 and 12 min are listed in Table 3.1. As it is seen in Table 3.1, zeta potential and surface tension of MWCNT suspension subjected to

the different time of ultrasonication remained on the same level. Thus, the time of ultrasonication does not have an impact on the zeta potential and surface tension of MWCNT suspension. It means that, as for particle size testing, the ultrasonication time of 6 min can be taken as optimal time with applied ultrasonication equipment in chosen ultrasonication intensity.

Table 3.1. Zeta Potential and surface tension of suspension after different time of ultrasonication

Suspension designation	Time of ultrasonication, min	Surface tension, mN/m	Zeta potential, mV
S3	3	67	–52.09
S6	6	67	–51.29
S9	9	67	–54.46
S12	12	67	–53.24

The zeta potential and surface tension measurements were carried out to evaluate the stability of complex MWCNT suspension prepared in combination with Pl and their plasticizing efficiency in cement-based materials.

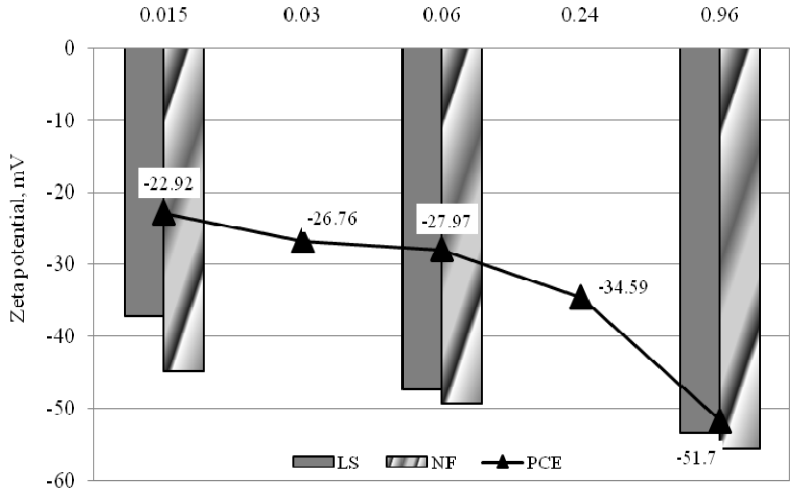


Fig.3.5. Zeta potential of suspensions with different plasticizing admixtures and multi-walled carbon nanotubes dosage

The LS, NF and PCE show the different extent of the changes in zeta potential. Fig. 3.5 presents the changes in the zeta potential of MWCNT suspensions with different Pl and MWCNT dosage. The increase in zeta potential by 30%, 19% and 56% for LS, NF and PCE plasticizers, respectively, was established with an increase of MWCNT dosage. The greater extent of the zeta potential changes was observed for PCE.

Possible changes in the zeta potential of MWCNT suspension with Pl of different origin can be associated with differences in their pH values.

The results of surface tension measurements for MWCNT suspension with and without Pl are presented in Fig. 3.6. The different chemical structure, pH values and genesis of Pl demonstrate the different values of surface tension.

Addition of MWCNT to the suspension with Pl does not cause significant changes in surface tension. The surface tension values of complex suspension based on MWCNT and Pl is mainly determined by the properties of Pl based polymers.

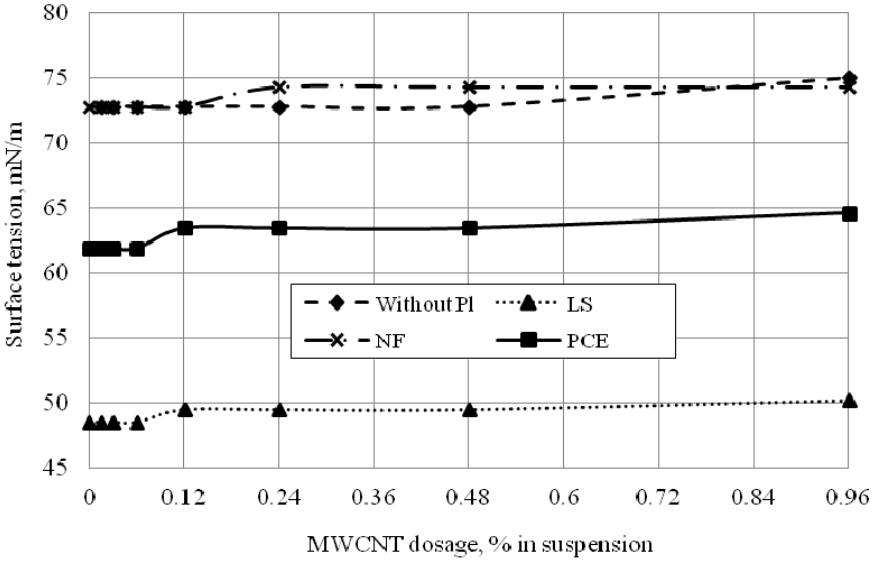


Fig.3.6. The surface tension of suspensions with different plasticizing admixtures and multi-walled carbon nanotubes dosage

The zeta potential and surface tension of complex suspension based on MWCNT and Pl are depending on properties of an applied Pl such as pH value and chemical structure.

3.1.3. pH and Electrical Conductivity Measurements

pH and electrical conductivity measurements were performed for MWCNT suspensions subjected to the ultrasonication for a different duration. The results of pH and electrical conductivity tests are presented in Table 3.2.

Table 3.2. pH and electrical conductivity after different time of ultrasonication

Suspension designation	Time of ultrasonication, min	pH	Electrical conductivity, mS/cm
S3	3	5.07	0.744
S6	6	5.05	0.754
S9	9	4.84	0.755
S12	12	4.87	0.698

The pH values changed from 5.07 to 4.87, with an increase of ultrasonication time from 3 to 12 min. It means that with an increase in ultrasonication time, the dispersion medium in the MWCNT suspension became more acid. This changes can be associated with the increase in dispersity of the MWCNT suspension in the homogenization process. The increase in dispersity causes enhancement of the interfacial surface between MWCNT and water molecules with a further increase in the concentration of H^+ counter ions which leads to the occurrence of the acid character in the MWCNT suspension.

As it is seen in Table 3.2, the electrical conductivity of MWCNT suspensions after different time of homogenization did not change remarkably.

The results of pH and electrical conductivity measurements of MWCNT suspensions with Pl are shown in Fig. 3.7, and Fig. 3.8, respectively.

The MWCNT suspensions with PCE and LS in the different MWCNT dosage have the acid nature. The NF demonstrates the alkaline character. The addition of MWCNT to the suspension with LS leads to the decrease in acid character, pH value changed from 4.3 to 5.5. The combined usage of NF and MWCNT leads to the neutralization of the suspension with the change of pH value from 9.1 to 7.6. The pH values of MWCNT suspension in the presence of PCE with the increase of MWCNT dosage up to 0.96% did not lead to the significant changes in pH values. Mainly, the observed character of MWCNT suspension with different Pl can be explained by differences in the chemical structure of Pl. The interaction of MWCNT and CMC (used as a dispersing agent in MWCNT suspension) with ions of Pl and water molecules changes the dispersity of the suspension with consequent changes in concentration of H^+ and OH^- counter ions and the changes in pH value.

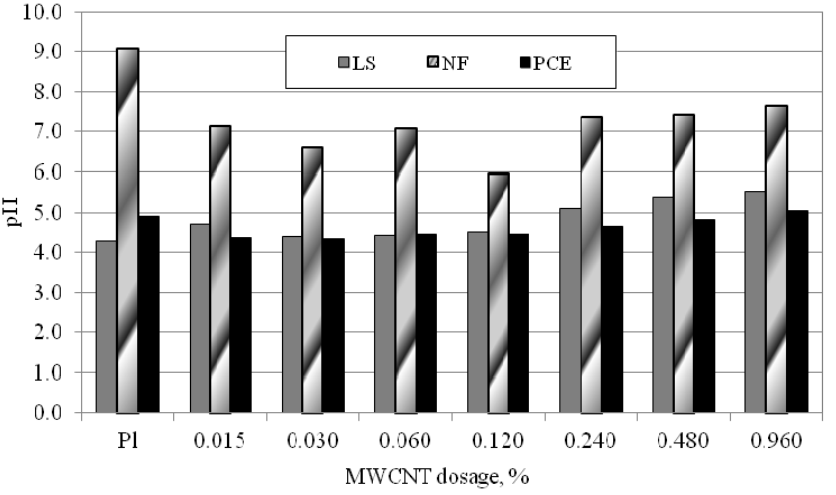


Fig.3.7. pH of suspension with plasticizing admixture

The electrical conductivity of suspensions with the increase of MWCNT dosage up to 0.96% in the suspension with LS and NF increased from 1.93 to 2.76 mS/cm and from 3.59 to 5.03 mS/cm, respectively.

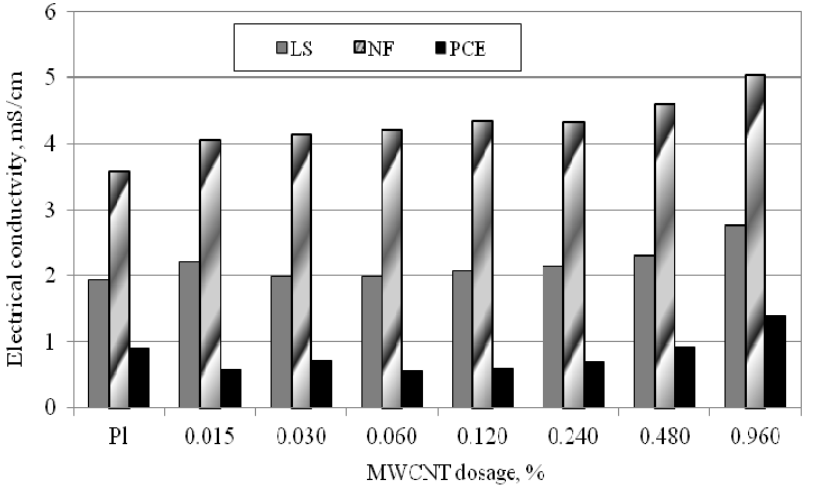


Fig.3.8. Electrical conductivity of suspension with plasticizing admixture

The variation of MWCNT dosage from 0.48 to 0.96% in the suspension with PCE increase the electrical conductivity from 0.91 to 1.40 mS/cm. The increase in electrical conductivity is associated with the presence of higher electrical charges on the MWCNT surface caused by the higher MWCNT concentration in the suspension and high electrical conductivity of MWCNT fibres. However, it should be noted that the addition of MWCNT in the dosage from 0.015 to 0.24% to the suspension with PCE decreases the electrical conductivity from 0.91 to 0.70 mS/cm.

This phenomenon can be explained as follows. The pellets "Graphistrength CW 2-45" contain 55 wt% of CMC, which is a polyelectrolyte with carboxylate groups. CMC dissociates in the aqueous medium to $RCOO^-$ and Na^+ ions. The intermolecular interaction between PCE and CMC can be the reason for a possible decrease in the mobility of ionic molecules and a further decrease in electrical conductivity. Usage of LS and NF with another chemical structure did not lead to a decrease in electrical conductivity. The results of the electrical conductivity test are presented in Fig. 3.8.

pH value and electrical conductivity of MWCNT suspensions do not depend significantly on the ultrasonication time. The addition of Pl to MWCNT suspension changes their pH with an increase of MWCNT dosage. The observed phenomenon can be linked with the interaction of MWCNT, ions of Pl of different chemical genesis and water molecules, which changes the dispersity of the suspension with consequent changes in concentration of H^+ and OH^- counter ions. The electrical conductivity of MWCNT suspension in the presence of various Pl increased with an increase of MWCNT dosage caused by higher MWCNT concentration and electrical charges on the MWCNT surface.

3.1.4. Characterization of Suspension during the Ageing Process

The MWCNT suspension has the high dispersity and aims to the coagulation of small particles. The MWCNT suspension with PCE was tested after one month of ageing in the course of the research. The pH, electrical conductivity and particle size analysis were performed to evaluate the properties of MWCNT suspension after one month of ageing.

Fig. 3.9 presents the pH values of MWCNT suspension. pH values of MWCNT suspensions with an increase of MWCNT dosage from 0 to 0.96% decreased. The pH value of MWCNT suspension with MWCNT dosage of 0.96% decreased from 5.0 to 4.7 after one month of ageing. MWCNT possess by the double electric layer around them. They create the ionic environment in a dispersion system according to counter ions. The decrease of pH level can be linked

with reduction in an interfacial surface between MWCNT and water molecules and a consequent reduction of the OH^- counter ions concentration caused by the coagulation processes in the MWCNT suspension during the ageing.

The electrical conductivity of MWCNT suspension changed not significantly during the ageing, as it is seen in Fig. 3.9.

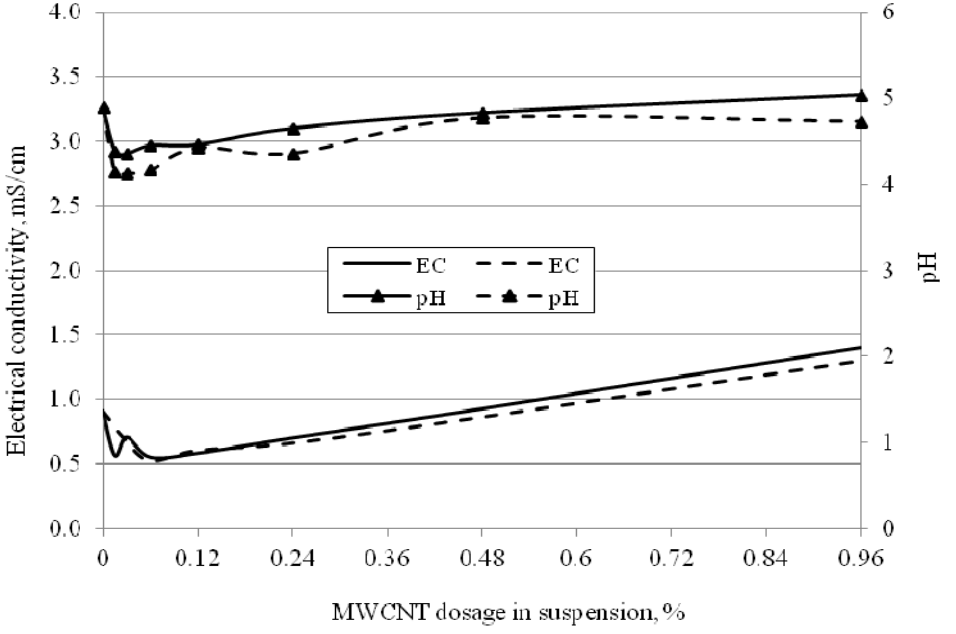


Fig.3.9. pH and electrical conductivity of suspension with polycarboxylate ether plasticizier after ultrasonication (continuous line) and after ageing (dash line)

In addition to the pH and electrical conductivity (EC) measurements, the particle size analysis of MWCNT suspension after one month of ageing was performed.

The particle size analysis of MWCNT suspension after the homogenization revealed that the diameter of MWCNT suspension particles in the presence of PCE was varied from 150 to 600 nm. The average diameter of particles was established equal to 376 nm. The results of particle size analysis are presented in Fig. 3.10. The test of MWCNT suspension with PCE after one month of ageing presents a variation of particle sizes in the range from 350 to 900 nm and average diameter about 515 nm that indicates the agglomeration processes in the MWCNT suspension.

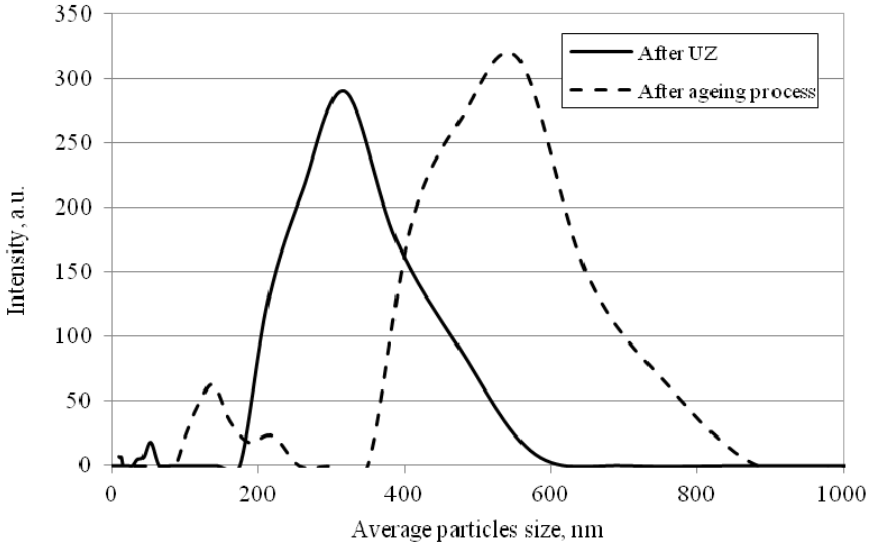


Fig.3.10. Particle size analysis of suspension after ultrasonication and after ageing

Based on the results of particle size analysis, pH and electrical conductivity measurements, it can be concluded that the homogenized MWCNT suspension is subjected to the coagulation processes in the volume after one month of ageing. Therefore, the modification of cement-based materials by MWCNT suspension should be provided directly after homogenization of MWCNT suspension.

3.1.5. Mechanism of the Interactions between nanotubes and Plasticizers in the Suspension

The action mechanism of MWCNT in the aqueous suspension with and without PL can be explained from the physical and chemical points of view.

From the physical point of view, the zeta potential is one of the main parameters which gives information about the stability and character of the interaction between particles of the dispersion phase in the MWCNT suspension. Fig. 3.11 presents the occurrence of zeta potential in MWCNT suspension.

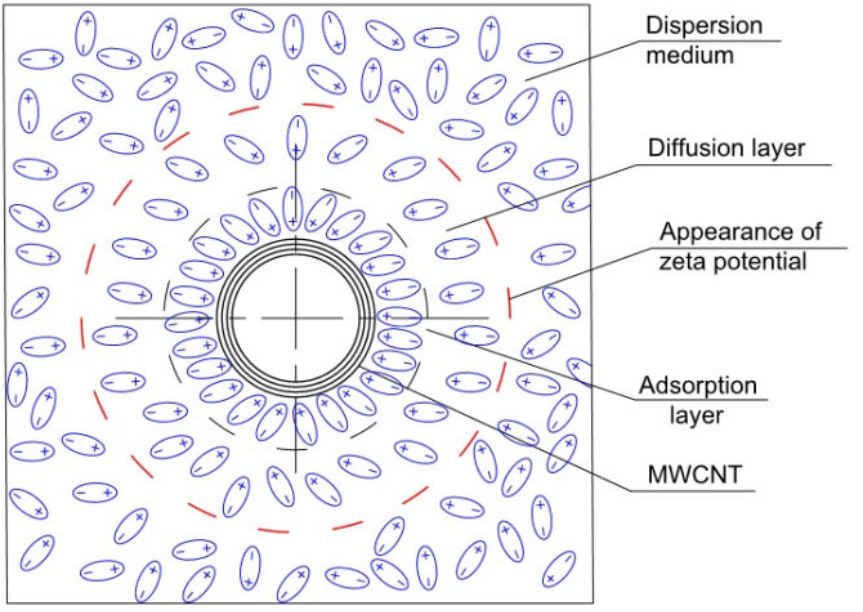


Fig. 3.11. Zeta potential in suspension of nanotubes

MWCNT suspension is a dispersion system where the distilled water is a dispersion medium, and MWCNT is a dispersion phase. MWCNT suspension, as a dispersion system, is characterized by the occurrence of the double electric layer on the interface of MWCNT and dispersion medium. MWCNT have the layer of the potential-determining ions on the surface, which form the adsorption layer with diffusion layer around. Zeta potential is presented on the boundary of the adsorption and diffusion layer. The presence of the double electric layers around the MWCNT surface can be a reason for the physical interactions of MWCNT with other components of MWCNT suspension.

Non-covalent functionalization of CNT as it is presented in Fig. 1.11 (section 1.3) leads to changes in zeta potential.

In the current research, MWCNT is covered by CMC. The presence of anionic groups of CMC on the MWCNT surface allows to disperse them by the repulsive forces. Fig. 3.12c schematically presents the interaction between MWCNT with anionic groups of CMC. The presence of CMC can explain the working mechanism of MWCNT in the suspension from the chemical point of view.

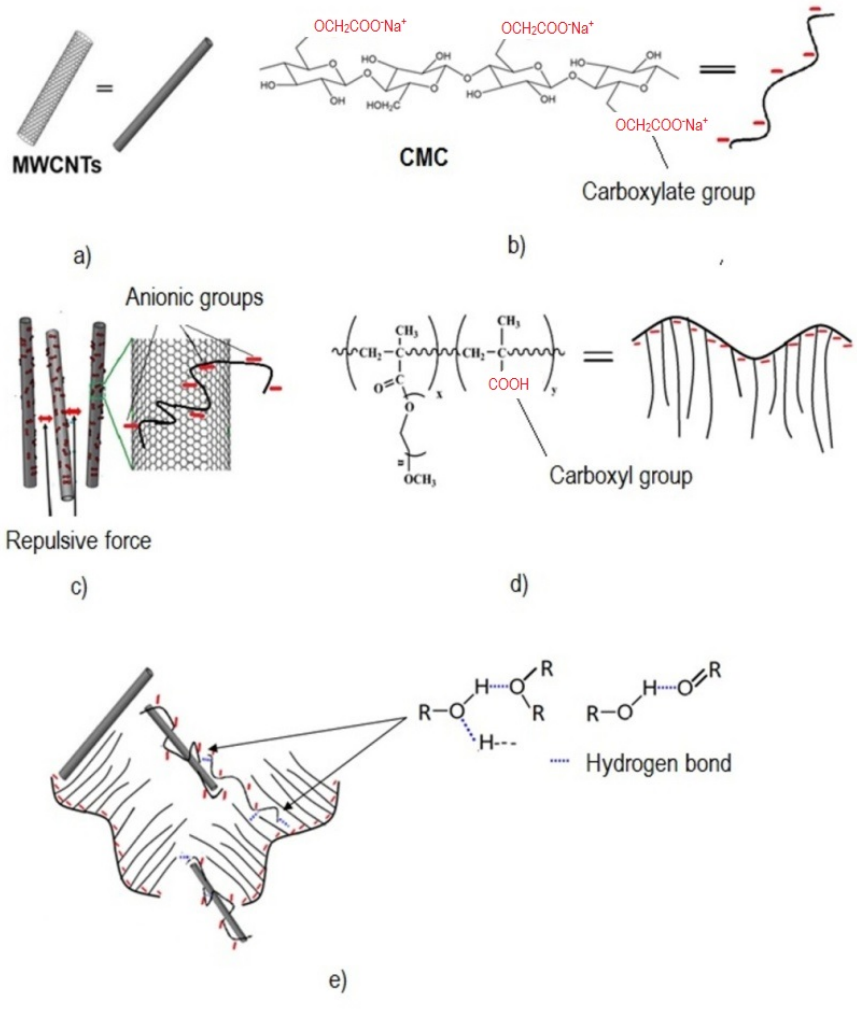


Fig. 3.12. Scheme of the interaction of polycarboxylate ether plasticizer and multi-walled carbon nanotubes with carboxymethyl cellulose: a) multi-walled carbon nanotubes; b) chemical structure and scheme of carboxymethyl cellulose; c) carboxymethyl cellulose on the carbon nanotubes; d) chemical structure and scheme of polycarboxylate ether plasticizer; e) formation of the hydrogen bond between carboxylate groups of the carboxymethyl cellulose on the carbon nanotubes surface and carboxyl groups of polycarboxylate ether plasticizer

In case of addition of Pl to MWCNT suspension, the chemical interactions between anionic groups of CMC and functional groups of Pl can explain the changes in the properties of MWCNT suspension.

The changes of zeta potential, average diameters of particles and electrical conductivity in MWCNT suspension with PCE, observed in the previous sections, can be caused by the intermolecular interactions between the carboxyl groups of the CMC located on the MWCNT surface and the carboxylate groups of PCE plasticizer, which form the hydrogen bonds. These interactions increase the number of anionic groups on the surface area of the particles and, as a consequence, promote aggregation of the particles. The proposed scheme of intermolecular interactions is presented in Fig. 3.12e.

The absence of the same effect in the case of LS and NF is caused by their different chemical structure and absence of carboxylate groups.

To confirm the chemical interactions in MWCNT suspension, FTIR spectroscopy was carried out for CMC, PCE, MWCNT pellets with CMC (designated as MWCNT) and MWCNT suspension with PCE (Fig. 3.13).

The following peaks were identified:

- the peaks in the range 3200–3600 cm^{-1} correspond to hydroxyl groups (–OH–) stretching (Sokrates 2001);
- the peak at about 2850 cm^{-1} is attributed to the symmetrical stretching vibration mode of –CH– (Cui *et al.* 2017);
- the peak 1732 cm^{-1} for PCE indicates the carbonyl group C=O stretching vibration (Sokrates 2001; Zhou *et al.* 2011b);
- the peak at about 1600 cm^{-1} (1634 cm^{-1} and 1638 cm^{-1}) point out the carbonyl groups C=O stretching vibration (Sokrates 2001; Zhou et al. 2011);
- the peaks 1344 cm^{-1} and 1385 cm^{-1} are caused by C–H stretching (Sokrates 2001; Cui *et al.* 2017);
- the peaks in the range 1000–1200 cm^{-1} corresponds to the vibration of the ether groups (–O–) of polymers (Sokrates 2001; Asl *et al.* 2017).

The homogenization of MWCNT suspension in combination with PCE leads to the following changes. The peak in the range 3200–3600 cm^{-1} increased with addition MWCNT in comparison with the sample only with PCE. This changes can be explained by the formation of hydrogen bonds between functional groups of PCE and CMC, which is used as a dispersing agent for MWCNT suspension.

The changes in hydrogen bonds between MWCNT with CMC and functional groups of Pl explain the increases in plastic viscosity of cement paste and the prevention of the increase in plastic viscosity after time as it is described in section 3.2.

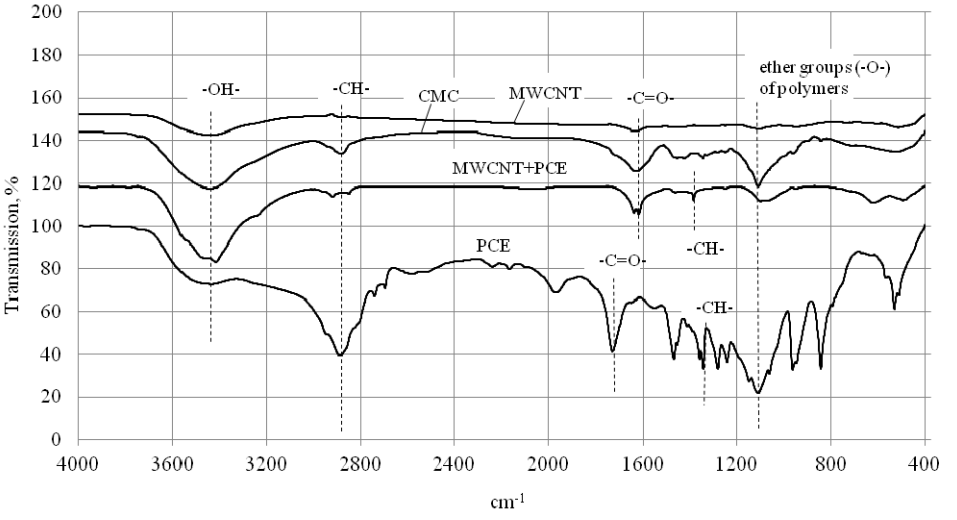


Fig. 3.13. Fourier-transform infrared spectroscopy of carbon nanotubes, carboxymethyl cellulose, polycarboxylate ether plasticizer and carbon nanotubes suspension with polycarboxylate ether

The interactions between functional groups of CMC and PCE are confirmed by the changes in the intensity of peaks at about 2850 cm^{-1}; the removal of the peak 1732 cm^{-1} typical for PCE; the occurrence of the peaks of C=O stretching at 1638 cm^{-1}; the decrease in the intensity of peaks 1385 cm^{-1} and 1099 cm^{-1} in comparison with PCE.

The attractive, repulsive forces and presence of the double electric layer explain the action mechanism of MWCNT in the suspension physically. The modification of MWCNT surface by CMC and their interaction with Pl through the functional groups can be a reason for chemical interactions in the MWCNT suspension.

3.2. The Influence of MWCNT on the Plasticizing Effect in the Cement Pastes

3.2.1. The Results of the Rheological Test of Modified Cement Pastes

The rheological parameters were obtained based on the approximation of experimental flow curves according to the Herschel-Bulkley rheological model. The experimental rheological curves are presented in Annex A. The approximation equations are attached in Annex B.

The present section represents the results of the rheological testing of the cement pastes modified by MWCNT suspension in different dosage with and without Pl. Based on the rheological parameters, obtained in the course of the approximation of the experimental flow curves, the dependence between the MWCNT dosage and rheological parameters, such as yield stress, plastic viscosity, shear thinning/ thickening indexes were established.

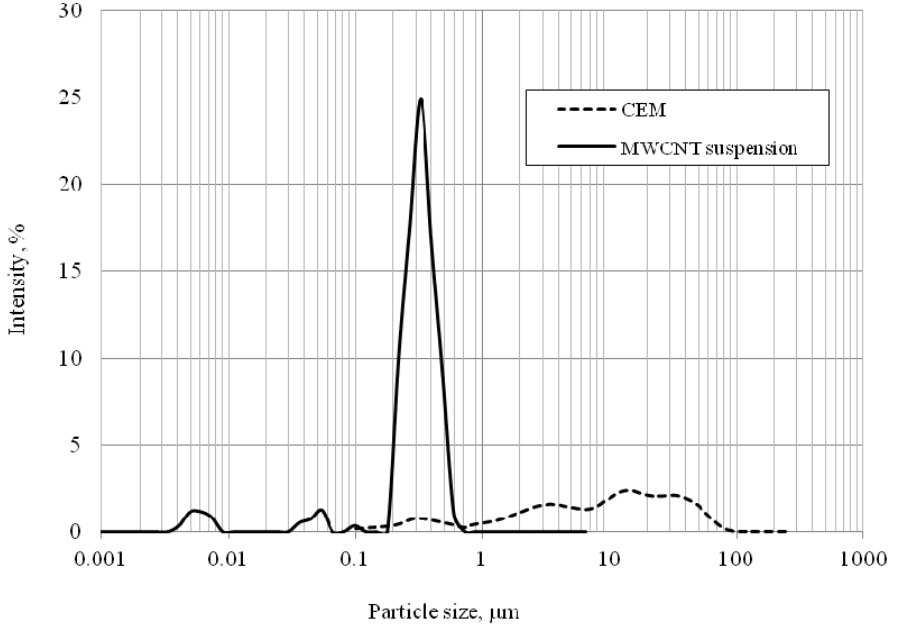


Fig. 3.14. The particle size distribution of Portland cement without mineral additives and suspension of carbon nanotubes

One of the factors which determine the rheological properties of cement-based materials is their particle size. Fig. 3.14 demonstrates the results of particle size analysis for Portland cement without mineral additives and MWCNT suspension. The main content of particles of cement is placed in the range from 1 to 80 μm in size with an average value of cement particles size about 14.28 μm. In addition to particle size analysis, the Blain test was performed for applied cement and revealed the fineness of 3552 cm^2/g. The continuous curve in Fig. 3.14 presents the particle size distribution for MWCNT suspension. The main content of particle is placed in the range from 0.1 to 1 μm with an average diameter of nanoparticles of 293 nm (0.293 μm). It can be concluded that cement particles have a size in 50 times more than one for MWCNT suspension. Such difference in size has one of the key roles in changes of the rheological parameters of the cement pastes with MWCNT which are presented below.

Fig. 3.15 shows the changes in yield stress of cement paste modified by MWCNT in the dosage from 0 to 0.24% bwoc. The diagram indicates that yield stress increased with an increase of MWCNT dosage. The maximum increase in the yield stress by 17% was obtained for the cement paste modified by 0.24% bwoc of MWCNT in comparison with the reference cement paste without admixtures.

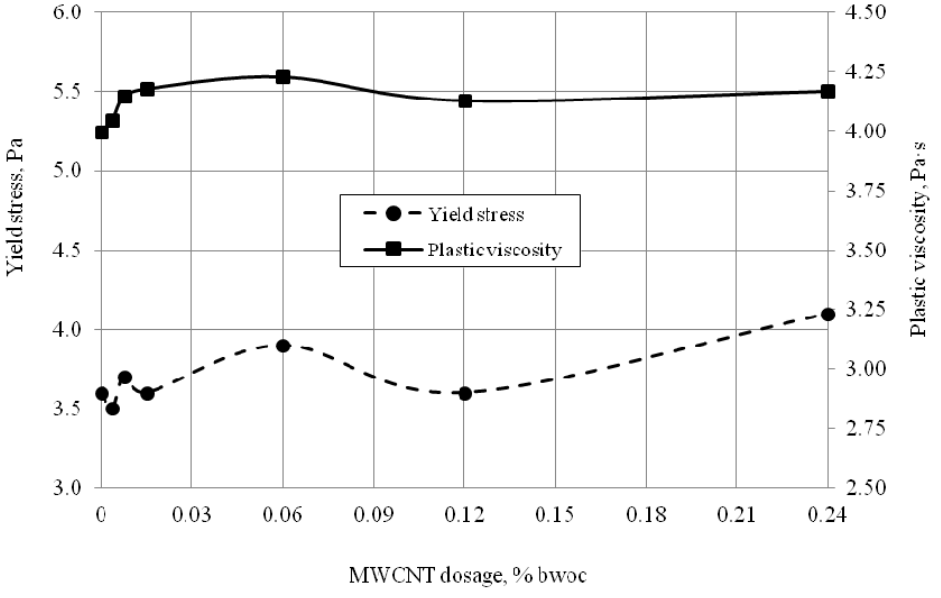


Fig. 3.15. Yield stress and plastic viscosity of cement paste modified by suspension

The addition of MWCNT in the dosage from 0 to 0.24% bwoc to the cement paste increased the plastic viscosity. The maximum increase in plastic viscosity by 6% was obtained for the cement paste modified by MWCNT in the dosage of 0.06% bwoc in comparison with the reference sample without admixture (Fig. 3.15).

The rheological parameters of the cement paste modified separately by CMC in the dosage of 0.29% bwoc were determined due to the presence of CMC in MWCNT suspension as a dispersing agent. The yield stress and plastic viscosity were of 3.2 Pa and 2.65 Pa·s in 5 min after cement paste mixing. These parameters are less than ones for the cement paste modified by the suspension with MWCNT dosage of 0.24% bwoc as 4.1 Pa and 4.17 Pa·s. It demonstrates that MWCNT leads to the additional increase in yield stress and plastic viscosity of cement paste in comparison with CMC.

Addition of MWCNT suspension in combination with LS to the cement paste led to the increase in yield stress (Fig. 3.16). The maximum increase in yield stress by 11% was reached for cement paste with MWCNT dosage of 0.24% bwoc in comparison with reference cement paste with LS.

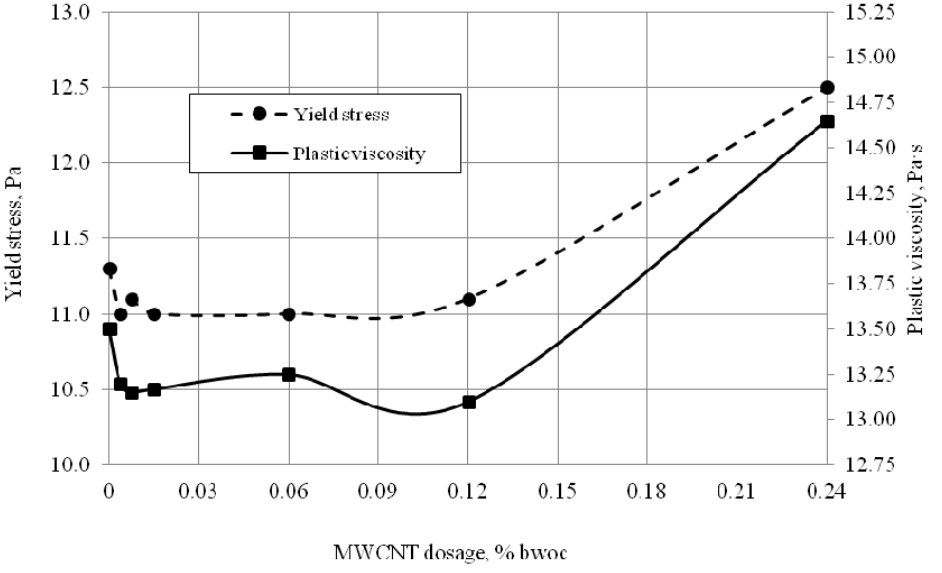


Fig. 3.16. Yield stress and plastic viscosity of cement paste modified by suspension and lignosulphonate plasticizer

The plastic viscosity of the cement pastes modified by MWCNT suspension with LS decreased up to the MWCNT dosage of 0.12% bwoc and started to increase over this dosage. The maximum increase in plastic viscosity by 9% for cement pastes modified by MWCNT suspension with LS was identified for the MWCNT dosage of 0.24% bwoc, as it is seen in Fig. 3.16.

The yield stress of cement paste modified by MWCNT suspension in combination with NF decreased by 11% with a variation of MWCNT dosage from 0 to 0.24% bwoc. The modification of cement paste by 0.24% bwoc of MWCNT resulted in the increase of the yield stress up to the reference value of yield stress (value for cement paste with NF).

The plastic viscosity of cement paste modified by MWCNT suspension with NF decreased up to 13% in the range of MWCNT dosage from 0 to 0.12% bwoc. The increase of MWCNT dosage from 0.12% to 0.24% bwoc resulted in the change of the plastic viscosity up to the value of plastic viscosity for the reference cement paste with NF (Fig. 3.17).

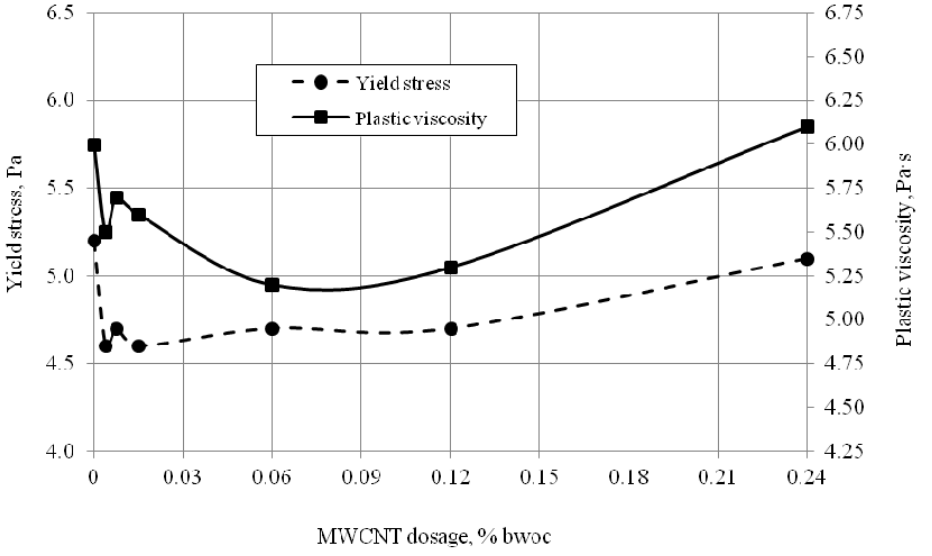


Fig. 3.17. Yield stress and plastic viscosity of cement paste modified by suspension and sulfonated naphthalene formaldehyde condensate plasticizer

Fig. 3.18 represents the changes in yield stress of cement paste modified by MWCNT in the dosage from 0 to 0.12% bwoc in the presence of PCE. The yield stress proportionally increased from the MWCNT dosage of 0.06% bwoc. The

maximum increase in yield stress value by 265% was obtained in the MWCNT dosage of 0.12% in comparison with a reference cement paste modified by PCE without MWCNT.

The proportional increase in the plastic viscosity of the cement paste modified by MWCNT suspension and PCE was observed from the MWCNT dosage of 0.015% bwoc up to 0.06% bwoc. Fig. 3.18 shows that the maximum increase by 107% was established for the cement paste modified by MWCNT dosage of 0.12% bwoc in presence of PCE.

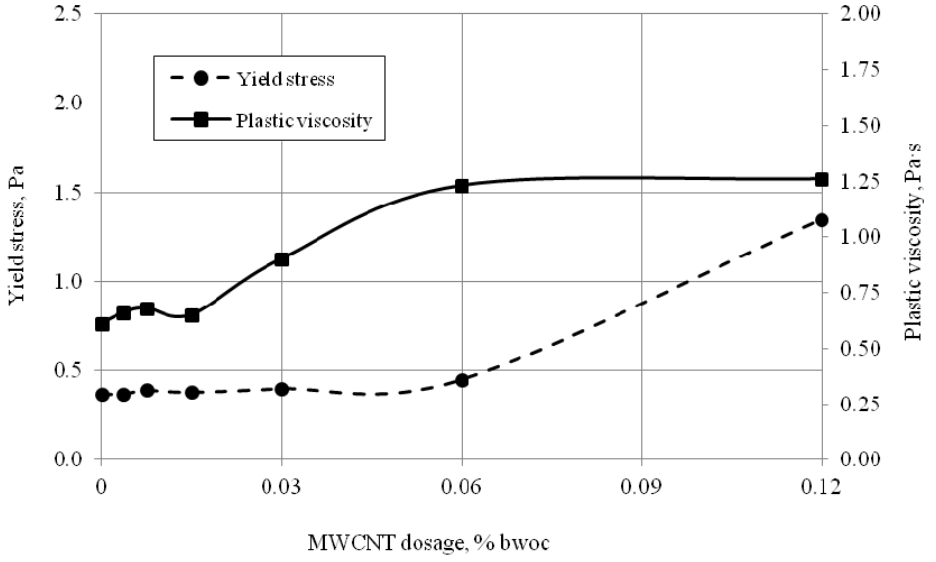


Fig. 3.18. Yield stress and plastic viscosity of cement paste modified by suspension and polycarboxylate ether plasticizer

In addition to the yield stress and plastic viscosity, the shear thinning/ thickening indexes of cement paste modified by MWCNT suspension with and without Pl were derived based on the approximation of the experimental rheological curves according to the Herschel-Bulkley rheological model.

The changes in the shear thinning/ thickening indexes depend on MWCNT dosage and type of Pl are shown in Fig. 3.19a and Fig.3.19b, respectively, in 5 min and 120 min after cement paste mixing. The cement paste without Pl and with LS and NF characterized by the shear thinning flow behaviour. In case of a complex modification of cement paste by MWCNT with LS and NF, the shear

thinning index slightly decreased from 0.70 to 0.64 and from 0.83 to 0.72, respectively, with the introduction of MWCNT up to 0.06% bwoc.

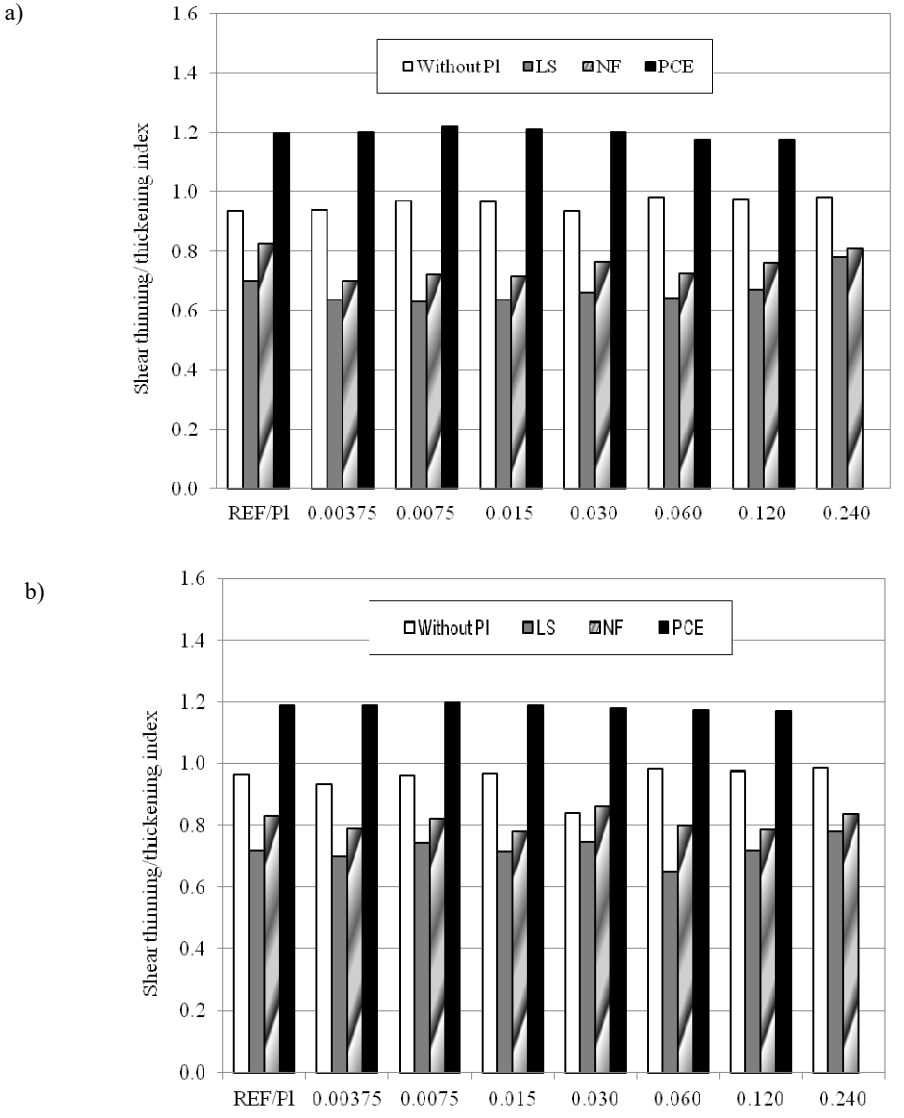


Fig. 3.19. Shear thinning/ thickening index of the cement paste modified by suspension and plasticizer in 5 (a) and 120 min (b) after cement paste mixing

Opposite to the effect of LS and NF, the nanomodified cement pastes with PCE represented the occurrence of shear thickening flow behaviour. With the increase of MWCNT dosage from 0 to 0.24% bwoc, shear thickening index of cement paste with PCE and MWCNT slightly decreased from 1.20 to 1.17.

The observation of shear thickening behaviour of PCE correlates with the results of the researches presented by Skripkiunas & Dauksys, 2004; Janavičius et al. 2013 and Yahia & Tanimura, 2015. Mainly, the shear thinning/ thickening indexes are determined by the type of Pl and does not depend significantly on MWCNT dosage. The increase of MWCNT dosage from 0 to 0.24% did not result in the changes in shear thinning/thickening indexes for cement pastes without Pl and with LS and NF. However, in the case of usage PCE, the shear thickening effect decreased with an increase of MWCNT dosage over 0.030% bwoc.

The shear thinning indexes slightly increased in 120 min after cement paste mixing in comparison with the indexes in 5 min after cement paste mixing for the samples with LS and NF. Modification of cement pastes by PCE did not cause the changes of shear thickening indexes in 120 min after cement paste mixing.

The rheological test of nanomodified cement pastes with and without Pl revealed the changes in yield stress, plastic viscosity and flow behaviour. The different chemical structures of Pl effect on the rheological properties of cement paste differently. The discussion about the action mechanism of Pl in combination with MWCNT suspension in the cement paste is described below in section 3.2.4.

3.2.2. The Influence of the Suspension on the Duration of the Plasticizing Effect

The rheological properties of cement paste modified by MWCNT suspension with and without Pl were tested in 5, 60 and 120 min after cement paste mixing to evaluate the plasticizing efficiency of the admixtures in time. The present section will demonstrate the dependence between yield stress, plastic viscosity, time after cement paste mixing and MWCNT dosage in the presence of different Pl.

Modification of cement paste by MWCNT suspension with and without Pl did not have a significant impact on the yield stress character in time after cement paste mixing. Fig. 3.20–3.23 show the changes in yield stress of nanomodified cement pastes with and without Pl in 5, 60 and 120 min after cement paste mixing.

Fig. 3.20 demonstrates that yield stress of cement paste modified by MWCNT suspension without Pl linearly increases for 120 min after cement paste. The character of dependence between yield stress and time after cement

paste mixing remained similar for all cement paste with MWCNT dosages varied from 0 to 0.24%. The changes in yield stress for 120 min after cement paste mixing did not exceed 10% for all tested cement pastes in comparison with samples after 5 min of mixing.

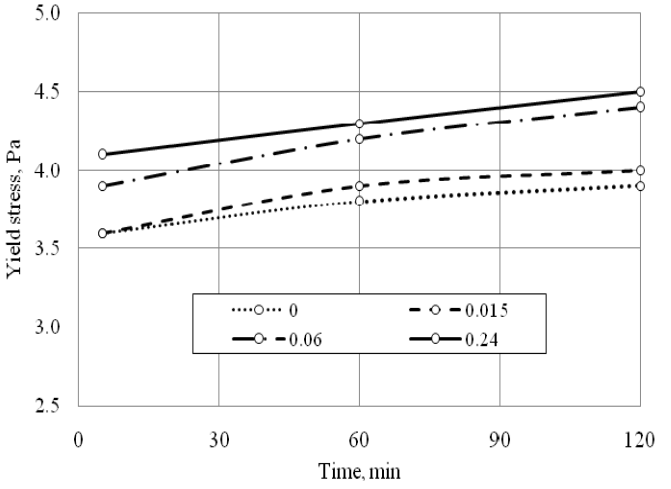


Fig. 3.20. Yield stress of cement paste modified by suspension in 5, 60 and 120 min after cement paste mixing

The yield stress of cement pastes modified by MWCNT suspension in combination with LS not remarkably increases from 5 to 120 min after cement paste mixing.

The increase in yield stress of cement paste in 120 min after cement paste mixing did not exceed 4% in comparison with yield stress in 5 min after cement mixing (0.24–curve in Fig. 3.21). The MWCNT dosage did not have an impact on the dependence between yield stress and time after cement paste mixing.

The usage of MWCNT suspension with NF (see Fig. 3.22) led to the proportional increase in yield stress during 120 min after cement paste mixing. The yield stress increased by 8% (reference cement paste with NF – 0–curve) and 20% (cement paste with MWCNT suspension with NF – 0.24–curve).

The yield stress of the cement paste modified by MWCNT suspension with PCE (see Fig. 3.23) did not change during 120 min after cement paste mixing (except 0.06 and 0.12–curves). The yield stress of the cement paste with PCE and MWCNT in the dosage of 0.06% bwoc slightly increased during 60 min after cement paste mixing and not significantly decreased after this time.

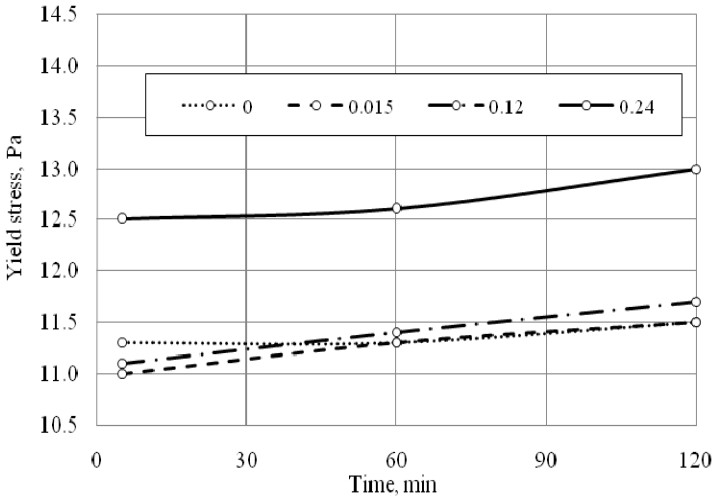


Fig. 3.21. Yield stress of cement paste modified by suspension and lignosulphonate plasticizer in 5, 60 and 120 min after cement paste mixing

The increase of MWCNT dosage up to 0.12% bwoc resulted in the decrease of yield stress from 60 to 120 min after cement paste mixing by 11% in comparison with cement paste in 5 min after mixing.

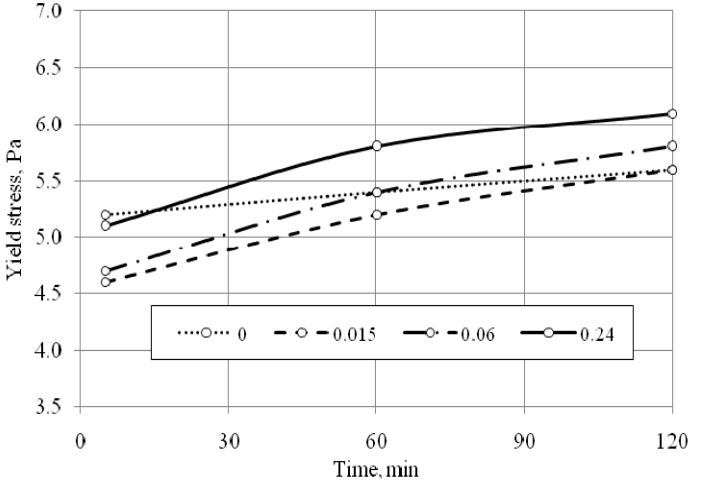


Fig. 3.22. Yield stress of cement paste modified by suspension and sulfonated naphthalene formaldehyde condensate plasticizer in 5, 60 and 120 min after cement paste mixing

The character of dependence between plastic viscosity and time after cement paste mixing had differences in the presence of Pl of various origin. The addition of MWCNT to cement paste did not have any impact on the dependence between plastic viscosity and time after cement paste mixing.

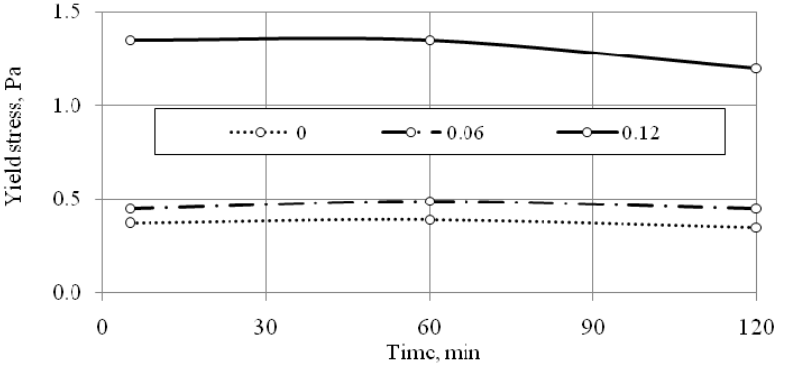


Fig. 3.23. Yield stress of cement paste modified by suspension and polycarboxylate ether plasticizer in 5, 60 and 120 min after cement paste mixing

Fig. 3.24 represents the dependence between plastic viscosity and time after cement paste mixing in case of a modification of cement paste by MWCNT in the dosage from 0 to 0.24% bwoc.

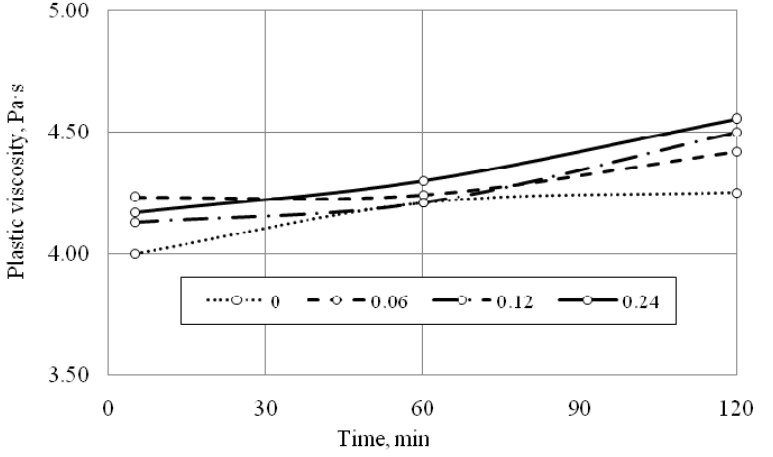


Fig. 3.24. Plastic viscosity of cement paste modified by suspension in 5, 60 and 120 min after cement paste mixing

The plastic viscosity linearly increased from 5 to 120 min after cement paste mixing. The increase in plastic viscosity during the time by 6% and 8% were identified for cement pastes without admixture (0–curve) and MWCNT dosage of 0.12% bwoc, respectively. The same character of curves was observed for cement pastes with other MWCNT dosages.

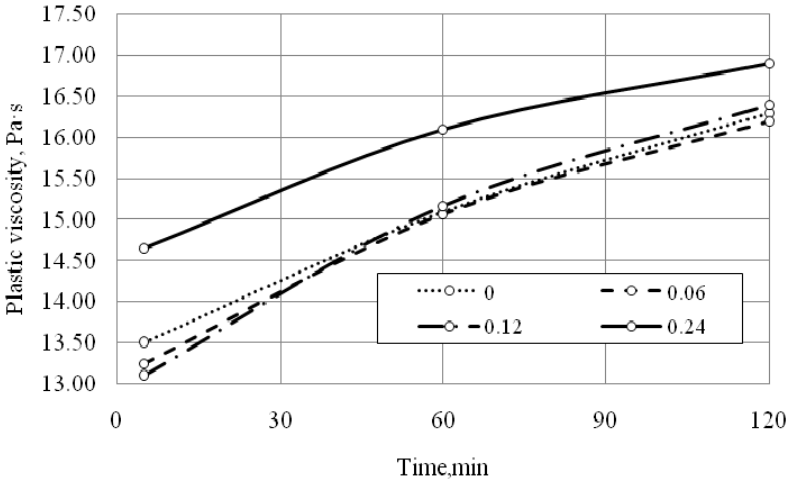


Fig. 3.25. Plastic viscosity of cement paste modified by suspension and lignosulfonate plasticizer in 5, 60 and 120 min after cement paste mixing

The cement pastes with MWCNT suspension and LS were characterized by a remarkable increase in plastic viscosity in the first 60 min after cement paste mixing (Fig. 3.25). The plastic viscosity increased by 21% for the reference cement paste with LS (0–curve) and by 15% for the cement paste modified by 0.24% bwoc of MWCNT (0.24–curve) in 120 min after cement paste mixing in comparison with values of plastic viscosity in 5 min. The character of curves for the cement paste with MWCNT dosage less than 0.24% bwoc was the same as for reference sample only with LS.

The plastic viscosity of cement pastes modified by MWCNT suspension and NF linearly increased from 5 to 120 min after cement paste mixing. The plastic viscosity of the reference cement paste with NF (0–curve) enhanced by 8% during 120 min after cement paste mixing. The maximum increase in the plastic viscosity by 23% during 120 min after cement paste mixing was established for the cement paste modified by 0.06% bwoc of MWCNT (0.06–curve). The other MWCNT dosages led to the increase in the plastic viscosity of cement pastes during the time after cement paste mixing no more than 9% in comparison

with values of the plastic viscosity in 5 min after cement paste mixing (Fig. 3.26).

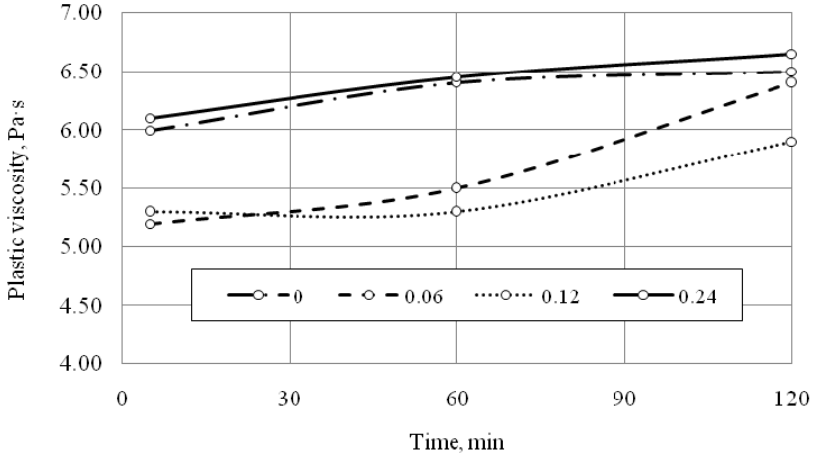


Fig. 3.26. Plastic viscosity of cement paste modified by suspension and sulfonated naphthalene formaldehyde condensate plasticizer in 5, 60 and 120 min after cement paste mixing

The modification of cement pastes by MWCNT suspension and PCE did not lead to the remarkable changes in plastic viscosity during the time after cement paste mixing (Fig. 3.27).

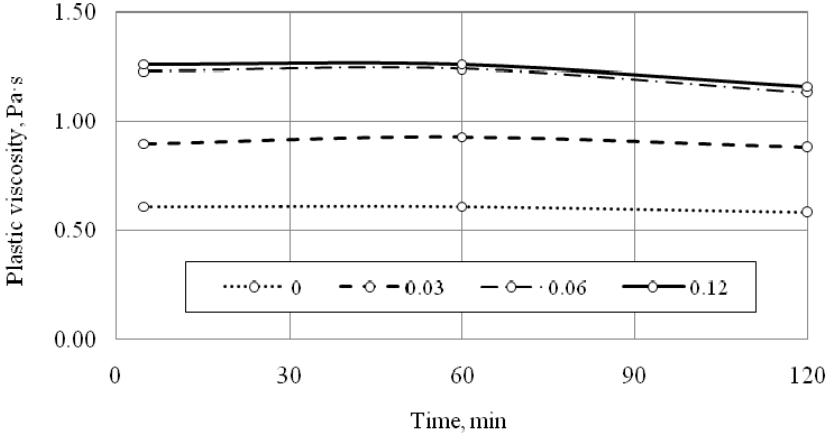


Fig. 3.27. Plastic viscosity of cement paste modified by suspension and polycarboxylate ether plasticizer in 5, 60 and 120 min after cement paste mixing

The plastic viscosity of the cement pastes with PCE and MWCNT in the dosage of 0.03%, 0.06% and 0.12% did not change during first 60 min after cement paste mixing and decreased by 8% during the next 60 min (0.06 and 0.12– curves).

The yield stress of cement paste modified by MWCNT suspension with and without Pl changed not remarkably in 120 min after cement paste mixing. The type of Pl had a significant effect on the plastic viscosity of cement-based materials in time after cement paste mixing. The addition of MWCNT in the dosage from 0 to 0.24% bwoc to the cement pastes did not lead to the noticeable changes in the character of the dependence between yield stress (plastic viscosity) and time after cement paste mixing.

3.2.3. The Influence of the Suspension on Water Bleeding of Cement Pastes

In addition to the rheological test, the water bleeding of cement pastes modified by MWCNT suspension without and with different types of Pl was estimated. As it is seen in Fig. 3.28, the increase of MWCNT dosage in cement pastes with all Pl contributed to the reduction of the volume coefficient of water bleeding. Water bleeding did not change up to the MWCNT dosage of 0.12% bwoc and decreased in the dosage of 0.24% bwoc for cement paste without Pl. The decrease in the volume coefficient of water bleeding was of 85% in comparison with the reference sample without MWCNT modification.

The addition of Pl led to more liquid consistency of the cement-based materials and more significant water bleeding in comparison with samples without Pl. The volume coefficient of water bleeding in cement pastes with LS, NF and PCE remarkably reduced up to the MWCNT dosage of 0.015% bwoc and gradually reduced over this dosage. The reduction of the volume coefficient of water bleeding reached the values of 99%, 100%, 83% for LS, NF and PCE, respectively, with an increase of MWCNT dosage up to 0.24% bwoc. The volume coefficient of water bleeding reached the values closer to 0 with the MWCNT dosage of 0.24% bwoc in cement-based materials without Pl, with LS and NF.

Taking into account the presence of CMC in the MWCNT suspension, the water bleeding test was performed for the cement-based materials modified by CMC separately and CMC with PCE. Fig. 3.29 shows the water bleeding test for reference sample without any admixtures, for cement-based materials with CMC, PCE, CMC with PCE and MWCNT suspension (with PCE). The MWCNT dosage was of 0.06% bwoc in this experiment. The CMC dosage in accordance with MWCNT dosage was of 0.07% bwoc.

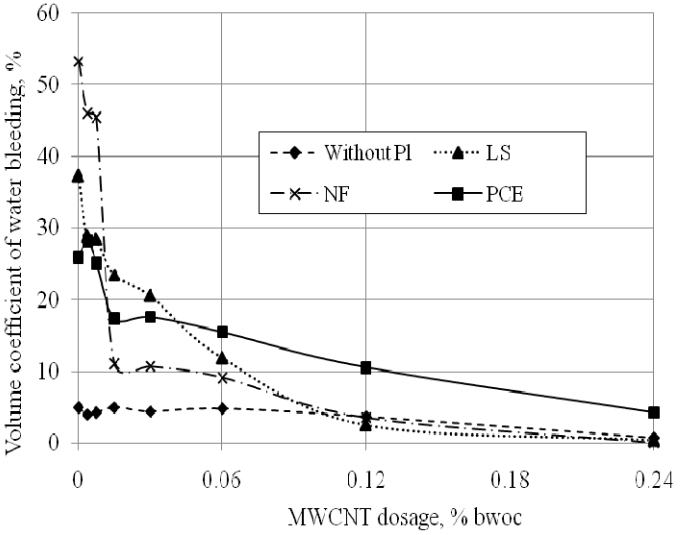


Fig.3.28. Water bleeding of nanomodified cement pastes with and without plasticizing admixture

The water bleeding test (see Fig. 3.29) revealed that addition of PCE leads to bleeding not only water but also a liquid phase with polymer (Fig. 3.29 c).

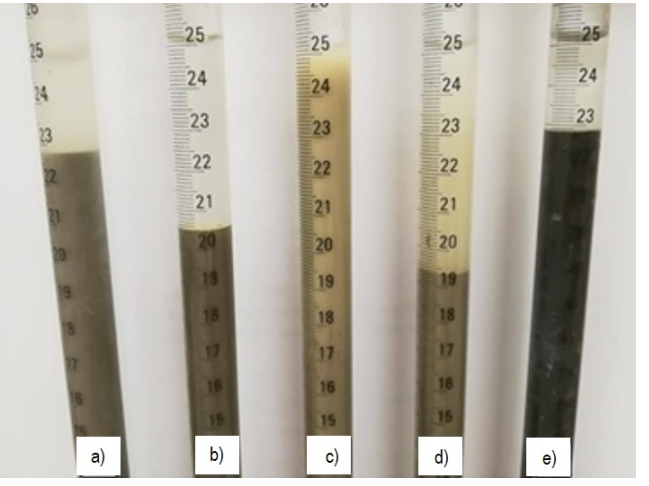


Fig. 3.29. Water bleeding test for cement pastes: a) without admixtures; b) with carboxymethyl cellulose; c) with polycarboxylate ether plasticizer; d) with carboxymethyl cellulose and polycarboxylate ether plasticizer and e) with suspension and polycarboxylate ether plasticizer

The complex modification by CMC and PCE results in the changes in bleeding liquid phase. Fig. 3.29d demonstrates light yellow colour of the liquid phase in comparison with the sample in Fig. 3.29c that can be linked with the formation of chemical bondings between functional groups of CMC and PCE. The cement-based materials modified by MWCNT suspension (which includes CMC as a dispersing agent) and PCE presents the absence of liquid phase like it was for samples in Fig. 3.29c and Fig 3.29d and value of bleeding water on the level of the reference sample (see Fig. 3.29a).

The results of the water bleeding test presented in Fig. 3.30 points out that the absorption of water in cement-based materials modified by MWCNT suspension and Pl are linked with the presence of MWCNT. CMC did not have an impact on the water bleeding and even slightly increase this parameter in all studied cement-based materials. It should be noted that MWCNT suspension (without Pl) and Pl in the course of this test was mixed manually in comparison with ultrasonication mixing of MWCNT and Pl in the test presented in Fig. 3.28. The correlation between the results in Fig. 3.28 and Fig. 3.30 can also highlight the necessity of the ultrasonication treatment for MWCNT suspension with Pl to obtain a more significant improvement of cement paste bleeding.

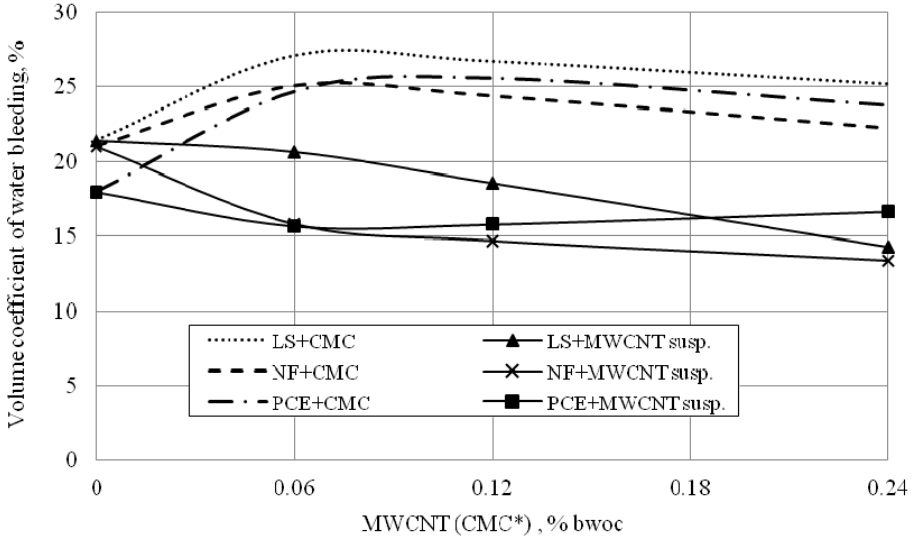


Fig. 3.30. Correlation between water bleeding of cement-based materials with carboxymethyl cellulose and with suspension in the presence of plasticizing admixture (carboxymethyl cellulose dosage was of 122% more than nanotubes dosage according to its content in "Grathistength CW 2-45" pellets)

The observed influence of MWCNT on the water bleeding of the cement pastes can be associated with high surface area and porous structure of MWCNT, which enable to retain water, decrease the level of free water and increase the physically bounded water content in cement-based materials. Moreover, the chemical bondings between functional groups of CMC and Pl should be taken into account as well. The action mechanisms of MWCNT in combination with Pl in the cement-based materials with results of FTIR spectroscopy for the confirmation of possible chemical interactions between components of the modified cement-based materials are presented in the following section and section 3.1.5.

3.2.4. The Action Mechanism of Nanotubes in Combination with Plasticizers in Cement Pastes

The action mechanism of the Pl in concrete is clear enough. The electrostatic and steric hindrance effects underlie the ability of Pl to prevent the flocculation and provide well dispergation of cement particles in concrete mixtures. Moreover, one of the main factors, which provide the plasticizing effect, is the decrease of surface tension on the surface of cement particles in mixing water with Pl (Collepardi 1998; Yoshioka *et al.* 1997; Chuang *et al.* 2019).

The electrostatic effect is more typical for Pl of the previous generation, such as LS and NF. This effect is provided by the adsorption of anionic polymers on the cement particles surface. The placement of negative charge of Pl on the cement particle leads to the changes of zeta potential in the cement paste and appearance of electrostatic repulsive forces between cement particles. The zeta potential measurements associate with electrostatic repulsive forces that allow making a conclusion about the plasticizing efficiency of Pl. The neutralization of the attractive forces between cement particles through the electrostatic repulsive forces facilitates the dispergation of cement particles and the increase of flowability of cement-based materials (Collepardi 1998).

The working mechanism of Pl of the last generation, such as PCE, is based on a steric hindrance and electrostatic effects. The number of researchers (Yoshioka *et al.* 1997; Chuang *et al.* 2019) highlighted the dominant character of the steric hindrance effect, which is provided by an extension of side chains in aqueous solution.

Fig. 3.31a and Fig. 3.31b present the scheme of interaction on the cement particles surface with and without Pl. The combined action mechanism of MWCNT and Pl in cement-based materials requires a deep investigation. MWCNT possess by high inner and outer surface area, porous structure and high aspect ratio, which can change the ordinary character of electrostatic and steric

effect of Pl. The proposed scheme in Fig. 3.31c presents the interaction on the cement surface particles in the presence of MWCNT and Pl.

The test of the rheological and technological properties may be used as an effective tool to investigate the plasticizing effect of MWCNT in cement-based materials and understand its working mechanisms. The MWCNT mechanism in cement paste may be explained by the following. The high surface area of MWCNT and their porous structure contribute to the remarkable adsorption and retention of water. The addition of MWCNT in specific dosages leads to the retention of water, which contributes to the increase in physically bounded water content in cement-based materials with a further increase in yield stress and plastic viscosity, in comparison with cement-based materials of the same W/C without MWCNT.

The high aspect ratio of MWCNT and their ability to form bundles may also influence the amount of physically bounded water and free water in the cement-based materials. The ability of MWCNT in some dosages to reduce the water content in cement-based materials decreases the plasticizing efficiency of Pl and, as a consequence, the flowability of cement paste. The rheological tests revealed that MWCNT addition with the achievement of a specific dosages increases the yield stress and plastic viscosity of cement paste (Reales *et al.* 2018). As for the rheological properties, the small size of MWCNT should be taken into account (see section 3.2.1, Fig. 3.14).

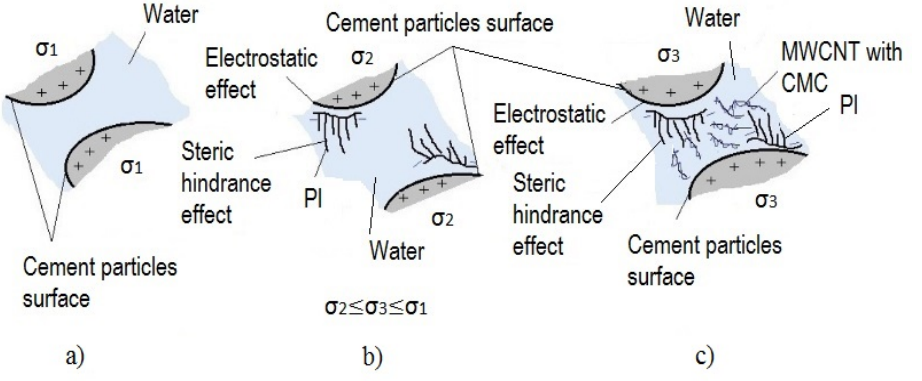


Fig. 3.31. Interaction on the cement particles surface: a) without admixtures; b) with plasticizing admixture; c) with plasticizing admixture and nanotubes, where σ is the surface tension on the surface of cement particles in mixing water with plasticizer

The applied dispersing agent (carboxymethyl cellulose (CMC) for MWCNT homogenization and Pl used in the cement-based materials should be taken into

account. The chemical bonds between dispersing agents, functional groups of Pl and ions of cement hydration products can form the complexes, which contribute to the thickening of cement mixtures. As it was mentioned earlier, the MWCNT suspension was homogenized based on pellets consisted of MWCNT and CMC. The MWCNT with molecules of CMC may chemically interact with cement hydration products. The first explanation of viscosity-enhancing effect in cement-based materials modified by MWCNT might be that Ca^{2+} ions are combined with several ethers (R–O–R), carboxylate (R–COO–) or carboxyl (–COOH) groups in Pl. In case of cement paste modification by PCE plasticizer, Ca^{2+} ions can also be combined with several groups in CMC or PCE molecules. In other words, the intramolecular interactions may take place between Ca^{2+} ions, PCE and MWCNT with CMC molecules.

The second explanation might be that ether groups and hydroxyl groups can polarize the water molecules to form the hydrogen bonds. The formed hydrogen bonds can crosslink several polymer molecules together and provide the increase in yield stress and plastic viscosity in cement-based materials modified by MWCNT suspension with PCE plasticizer. The proposed scheme of the chemical interaction between Ca^{2+}, molecules of CMC and PCE plasticizer is presented in Fig. 3.32. FTIR spectroscopy presented in Fig. 3.13 confirms the possible chemical interactions between functional groups of CMC and PCE.

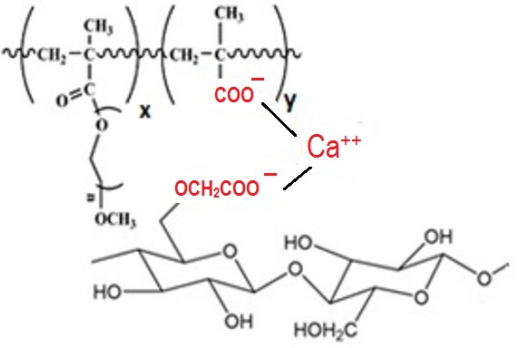


Fig.3.32. The scheme of chemical interaction between carboxymethyl cellulose, Ca^{2+} ions of cement paste and polycarboxylate ether plasticizer

The nanomodified cement paste without Pl and with LS, NF did not demonstrate the significant increase in yield stress and plastic viscosity. The observed phenomenon may be explained by the absence of carboxyl (–COOH) groups in LS and NF plasticizers that following by the increase in zeta potential (Huynh *et al.* 2006; Uchikawa *et al.* 1997). The absence of chemical interactions de-

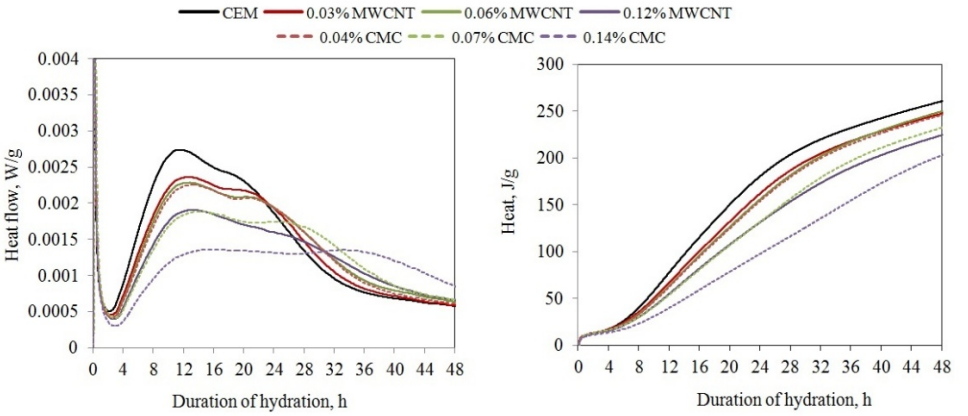
creases the effect of MWCNT and leads to not significant changes in rheological parameters of cement pastes with these admixtures.

Another important parameter of cement pastes which changes with the addition of MWCNT to cement paste is water bleeding. As it was observed from section 3.2.3, the increase in MWCNT dosage up to 0.24% bwoc noticeably decreases the volume coefficient of water bleeding in cement pastes with all kinds of Pl. The observed effect of MWCNT on the water bleeding of the cement pastes can be explained by the high surface area and porous structure of MWCNT, which can retain water, decrease the level of free water and increase the physically bounded water content in cement paste.

3.3. The Influence of the Suspension on the Cement Hydration Process

3.3.1. The Rate of Cement Hydration in Modified Cement-Based Materials

The calorimetric analysis with measurements of the heat evolution during the hydration process was performed to clarify the hydration processes which take place in nanomodified cement pastes with and without Pl.



a) b)

Fig. 3.33. Calorimetric curves of: a) heat flow and b) total heat in samples with different dosage of nanotubes and carboxymethyl cellulose

Fig. 3.33a presents the calorimetric curves of heat flow for the cement pastes modified by MWCNT suspension. The induction period of samples with MWCNT suspension was found to be longer than in the reference sample without suspension. This period increased by 36, 48 and 1 h 12 min for samples with MWCNT dosage of 0.03, 0.06 and 0.12% bwoc, respectively.

The acceleration period in samples with MWCNT suspension proceeds less intensively in comparison with a reference sample without suspension. It should be noted that the height of the peak in acceleration period for the samples with MWCNT suspension was lower than one for samples without it. The peak in acceleration period of the samples with MWCNT suspension occurred later on about 1 h for the MWCNT dosage of 0.03, 0.06% and on 1 h30 min for 0.12% bwoc, respectively, in comparison with the reference sample without suspension.

A shoulder at second deceleration process caused by aluminate hydration reaction and final formation of ettringite became more extended with the increase of MWCNT dosage up to 0.12% bwoc in comparison with this shoulder for the reference sample without admixtures. The peak at the second deceleration period was less noticeable with the increase of MWCNT dosage in comparison with the reference sample without suspension.

Fig. 3.33b presents that samples with an increase of MWCNT dosage emit less heat energy in comparison with the reference sample without suspension. The total heat emitted after 48 h of hydration decreased from 260.3 J/g to 224.2 J/g with an increase of MWCNT dosage from 0 to 0.12% bwoc. CMC also reduced the total emitted heat. CMC in the dosage from 0 to 0.14% bwoc reduced the total emitted heat from 260.3 J/g to 202.7 J/g. It should be noted that CMC led to a more noticeable reduction in total emitted heat in comparison with values for nanomodified samples.

The combined influence of MWCNT with Pl on cement hydration was tested as well. The calorimetric investigation was undertaken for the samples with 1% of LS and complex admixture based on MWCNT and LS. Fig. 3.34a and 3.34b present the calorimetric curves of heat flow and total heat, respectively.

The induction period of cement paste modified by MWCNT suspension and LS did not change in MWCNT dosage of 0.03% and 0.06% bwoc and prolongated by 1h for cement paste with MWCNT dosage of 0.12% bwoc in comparison with a reference sample (cement paste modified only by LS).

Addition of MWCNT suspension to the cement-based materials with LS decreased the height of the peak in acceleration period with the increase of MWCNT dosage from 0 to 0.12% bwoc which is higher for cement paste with LS. In addition to the height of the peak in acceleration period, MWCNT suspension prolongated the appearance of this peak by about 14 h with the increase of MWCNT dosage up to 0.12% bwoc. The shoulder of aluminate hydration reaction and ettringite formation was extended in comparison with the reference

sample (modified only with LS) with the increase of MWCNT dosage up to 0.12%.

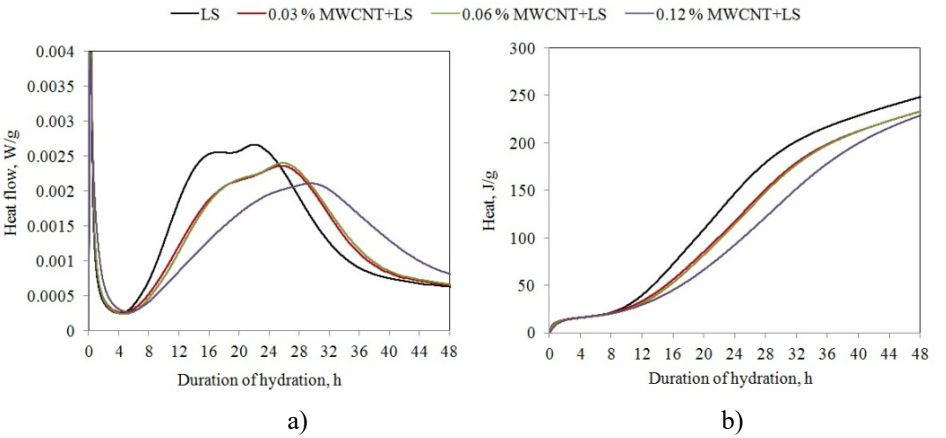


Fig.3.34. Calorimetric curves of: a) heat flow and b) total heat in samples with suspension and lignosulphonate plasticizer

According to the graph in Fig. 3.34b, the addition of MWCNT suspension to the cement pastes with LS decreases the emission of the heat energy in comparison with the sample only with LS.

The modification by MWCNT suspension with the increase of MWCNT dosage from 0 to 0.12% bwoc in the presence of LS led to a decrease of the total emitted heat after 48h of hydration of cement pastes from 248.2 J/g to 228.7 J/g which can be caused by the great value of retardation effect due to the high dosage of LS in cement paste.

Fig. 3.35a shows that the application of MWCNT suspension in the cement-based materials with NF causes the prolongation of the induction period of hydration by 30 min, 30 min and 1 h for MWCNT dosage of 0.03, 0.06 and 0.12% bwoc, respectively, in comparison with a reference sample (cement paste with NF without MWCNT suspension).

The peak of an acceleration period for cement-based materials with MWCNT suspension and NF slightly decreased (about 5%) in comparison with the sample modified by NF without MWCNT. The introduction of MWCNT suspension with MWCNT dosages of 0.03, 0.06 and 0.12% bwoc in the cement pastes with NF resulted in the later emergence of acceleration peak by 2 h, 3 h and 6 h, respectively, in comparison with reference cement paste with NF.

The increase of MWCNT dosage from 0 to 0.12% bwoc in the presence of NF caused the elongation of the shoulder with the occurrence of a more remarkable peak at the second deceleration period in comparison with reference sample modified only with NF. The observed effect identified the intensification of processes of aluminate hydration reaction and ettringite formation.

The samples with MWCNT suspension and NF emit less heat energy in comparison with the sample only with NF (Fig. 3.35b). The total heat emission did not change remarkably (from 240.7 J/g to 245.2 J/g) with the increase of MWCNT dosage from 0 to 0.12% bwoc.

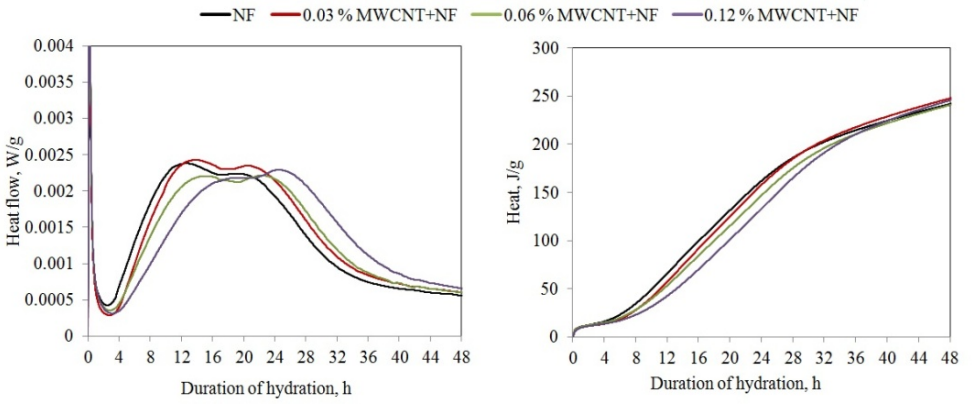
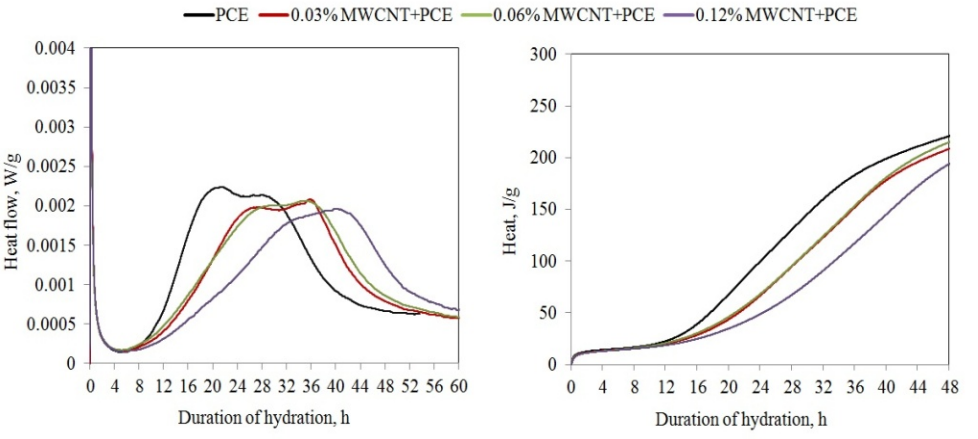


Fig. 3.35. Calorimetric curves of: a) heat flow and b) total heat in samples with suspension and sulfonated naphthalene formaldehyde condensate plasticizer

The introduction of MWCNT suspension with the increase of MWCNT dosage from 0 to 0.12% bwoc to the cement-based materials with PCE did not influence on the induction period of hydration, as it is seen in Fig. 3.36a. The acceleration period is characterized by the decrease of the height of the main peak in the case of usage of MWCNT in the dosage from 0 to 0.12% bwoc for modification of cement-based materials with PCE. Moreover, modification by the suspension with MWCNT in the dosage of 0.12% bwoc prolongs the occurrence of this peak by about 14 h in comparison with reference cement paste (cement paste only with PCE).



a) b)

Fig.3.36. Calorimetric curves of: a) heat flow and b) total heat in samples with suspension and polycarboxylate ether

The peak at the second deceleration period became upper than the peak at acceleration period with an increase of MWCNT dosage from 0 to 0.12%. This effect was not observed for the reference sample with PCE. Also, the shoulder at the second deceleration period was extended. The observed effects are linked with changes in aluminate hydration reaction and ettringite formation caused by the addition of MWCNT suspension.

The calorimetric curves of total heat presented in Fig. 3.36b identify the decrease in the heat energy emission with the addition of MWCNT in the range from 0 to 0.12% bwoc to the samples with PCE. The addition of MWCNT suspension to the cement paste with PCE leads to the decrease of total heat emission from 220.7 J/g to 193.8 J/g after 48 h of cement pastes hydration with an increase of MWCNT dosage up to 0.12% bwoc.

Hydration kinetics of cement paste modified by MWCNT suspension depends on not only the MWCNT dosage but also on the CMC dosage used as a dispersing agent for MWCNT suspension. To evaluate the impact of CMC on the hydration process, the calorimetry investigation of samples modified separately by CMC was performed. The addition of CMC in the dosage of 0.04% bwoc did not change the induction period of cement hydration and prolonged it by 1h for samples with CMC dosage of 0.07% and 0.14% bwoc in comparison with sample modified by MWCNT suspension (see Fig. 3.33a). The height of acceleration peak for samples modified by CMC was lower than one for samples with MWCNT suspension. Besides, CMC prolonged the occurrence

of the shoulder at the second deceleration process in comparison with the nano-modified cement pastes.

Table 3.3. Calculation of carboxymethyl cellulose impact on total emitted heat

MWCNT, % bwoc	CMC, % bwoc	Total emitted heat after 48 h, J/g		CMC impact, J/g
		Reference	CMC	
0.03	0.04	260.3	245.7	14.6
0.06	0.07		232.1	28.2
0.12	0.14		202.7	57.6

Take into account the total emitted heat for the reference sample (without admixtures) and samples modified by CMC, the CMC impact can be calculated as a difference between them. Table 3.3 present the calculation of CMC impact on total emitted heat after 48 h of hydration.

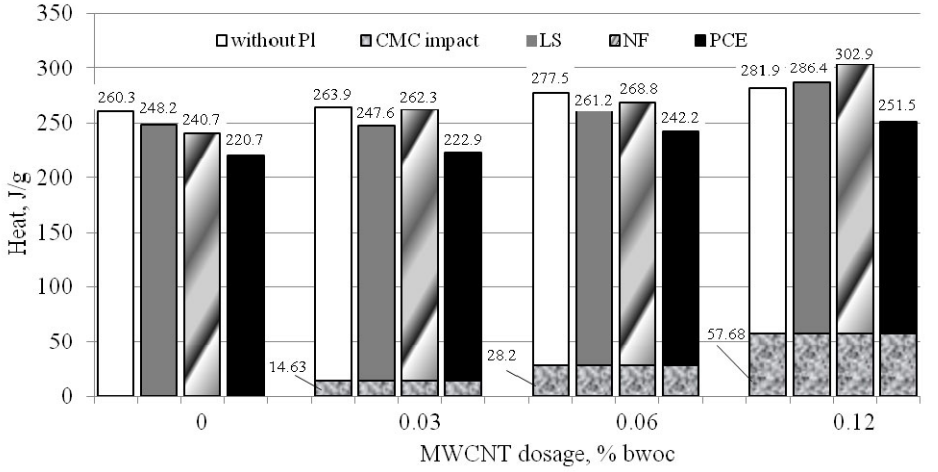


Fig. 3.37. Effect of nanotubes on the cement hydration heat emission after 48h

To summarize the CMC impact (see Table 3.1) and impact of MWCNT suspension and Pl on the total heat emission after 48 h of hydration (Fig. 3.33–3.36), the calculation of the separate impact of MWCNT on the cement hydration processes can be derived. Fig. 3.37 presents the total heat which can be emitted in case of the separate modification of cement paste by MWCNT. The increase of MWCNT dosage from 0 to 0.12% bwoc cause the increase in the total emitted heat for samples with and without Pl. The maximum increase by 21.6, 38.2, 62.2 and 30.8 J/g was obtained in case of modification by MWCNT in the

dosage of 0.12% bwoc without Pl and with LS, NF and PCE plasticizers, respectively.

3.3.2. The Setting Time of Modified Cement-Based Materials

In addition to the calorimetry test, the setting time test for cement paste with MWCNT suspension and CMC were undertaken. Results of setting time test for cement paste modified by MWCNT suspension and CMC are presented in Fig. 3.38.

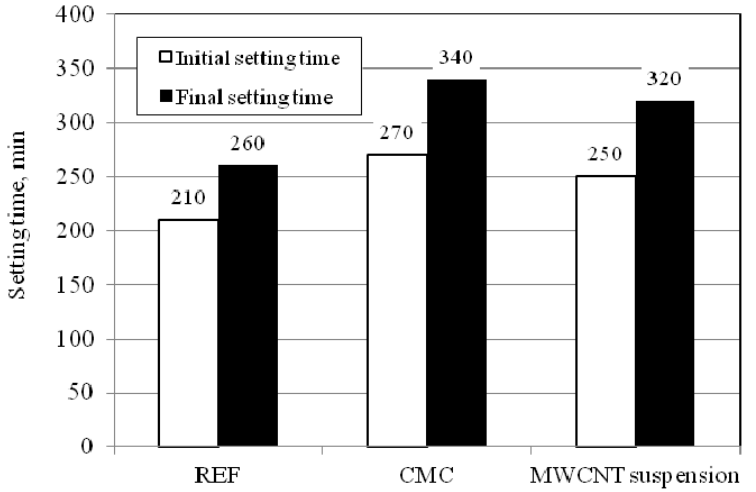


Fig. 3.38. Setting time of cement paste modified by carboxymethyl cellulose and suspension

Modification of cement paste by CMC resulted in the increase of initial and final setting time by 60 min and 80 min, respectively. Application of MWCNT suspension (with CMC) slightly decreased the initial and final setting time in comparison with sample modified by CMC. However, MWCNT suspension increases the initial and final setting time by 40 min and 60 min in comparison with reference cement paste without admixtures. The correlation of results presented in Fig. 3.33, 3.37 and Fig. 3.38 confirms the necessity to take into account the effect of CMC on the nanomodified cement-based materials in the hydration process.

3.4. Influence of Suspension on Microstructure of Cement-Based Materials

3.4.1. Phase Analysis of Cement Hydration Products

To clarify the formation of the hydration products in the nanomodified cement-based materials, X-ray diffraction (XRD), TG/DTG analysis and FTIR spectroscopy were performed.

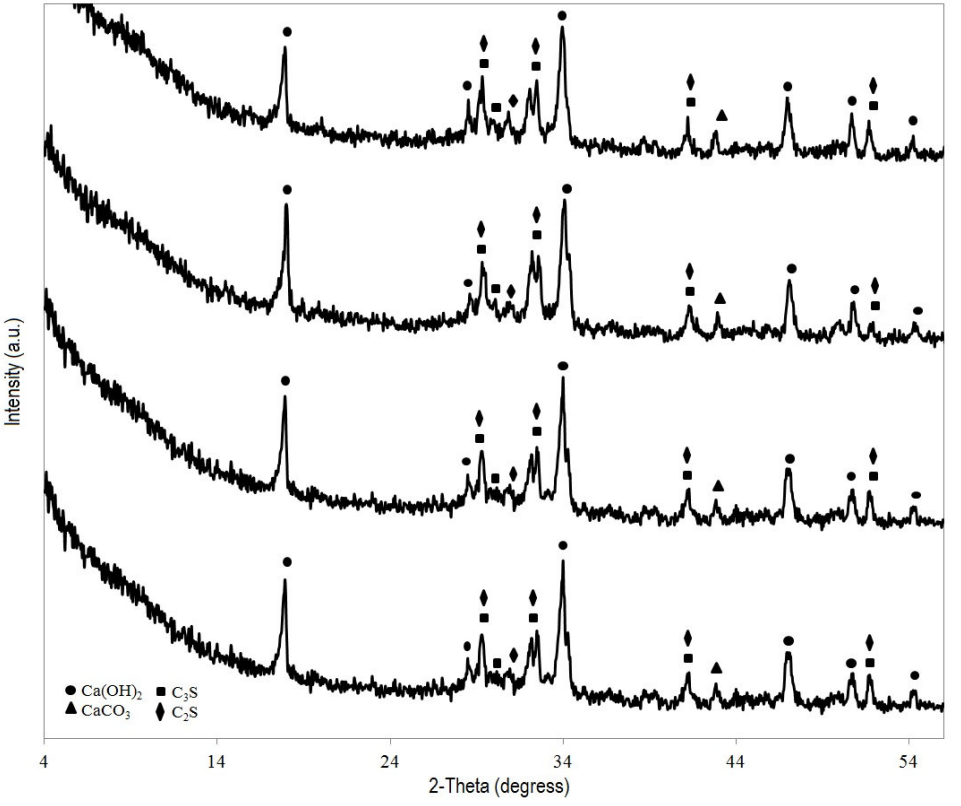


Fig. 3.39. X-ray diffraction patterns of cement samples with 0–0.12% bwoc of nanotubes

The XRD patterns of hardened cement paste modified by MWCNT in the dosage from 0 to 0.12% bwoc after 28 days of curing are shown in Fig.3.39.The identification of the peaks was performed by the usage of Highscore XRD Anal-

ysis software and literature sources (Trezza 2007; Tafesse & Kim 2019; Cui 2017). The XRD pattern of the reference cement paste indicated the formation of portlandite $Ca(OH)_2$, peaks of calcium carbonate $CaCO_3$ and the presence of C_3S and C_2S. It is difficult to determine the amorphous phases by XRD analysis, however the amorphous background in XRD patterns observed at $d = 0.257–0.310$ nm (28.7–35.0 2θ) can be linked with the presence of amorphous phases of calcium silicate hydrates (C-S-H).

The modification of cement paste by MWCNT in the dosage from 0 to 0.12% bwoc does not lead to the formation of new phases.

The quantitative Rietveld phase analysis of the cement samples revealed the different quantities of cement hydration products after the cement hydration process listed in Table 3.4.

Table 3.4. Quantitative Rietveld phase analysis

Phase	0% MWCNT	0.03% MWCNT	0.06% MWCNT	0.12% MWCNT
C_3S monoclinic (NISHI), %	8.26	9.11	10.70	11.07
C_2S beta (MUMME), %	8.85	8.34	8.13	7.33
C_3A cubic, %	1.38	1.09	0.70	0.69
C_4AF, %	2.05	2.62	1.41	2.27
Periclase, %	1.91	3.07	1.97	2.01
Calcite, %	1.94	3.12	2.73	3.62
Amorphous, %	48.43	47.10	50.70	50.31
Portlandite, syn, %	19.72	18.70	16.32	16.32
Brownmillerite, ferrian, syn, %	5.14	3.83	5.34	4.71
Dolomite, %	2.32	3.02	2.00	1.68

It is seen from Table 3.4 that addition of MWCNT in the dosage from 0 to 0.12% contributes to the increase of non-hydrated C_3S phase in hardened cement paste that means the decrease in C_3S hydration rate. The decrease in C_3S hydration rate causes the decrease of portlandite content in hardened cement paste. Moreover, cubic C_3A and C_2S phases are decreased in hardened cement paste that point out the increase of hydration rate of these phases and lead to the intensive formation of calcium hydroaluminates phase in hardened cement paste. The increase of non-hydrated C_3S phase from 8.26% to 11.07% can be linked with a decrease in the hydration rate due to the impact of CMC that is correlated with results of hydration kinetics presented above. The amorphous phase of nanomodified cement paste with an increase of MWCNT dosage up to 0.12% bwoc resulted in the enhancement from 48.43% to 50.31%, which can be explained by

the increase in the quantity of submicrocrystals (amorphous formations) formed during hydration of calcium silicate and calcium aluminate minerals.

According to the TG/DTG analysis in Fig. 3.40, the endothermic effects at 100–200 °C, 430–450 °C and 650–700 °C were identified. The peak at 100– 200 °C belongs to the dehydration of cement hydration products such as calcium silicate hydrates, calcium aluminium hydrates and ettringite. The second peak at 430–450 °C corresponds to the decomposition of portlandite. The last peak at the range of 650–700 °C is associated with the decomposition of calcite. The addition of MWCNT did not lead to the occurrence of new peaks for all MWCNT dosage.

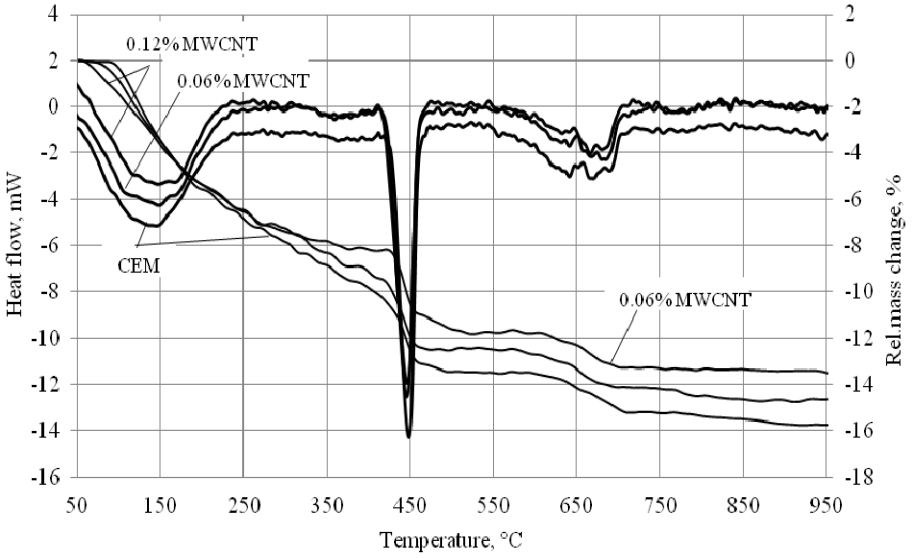


Fig. 3.40. Termal analysis of cement samples with 0–0.12% bwoc of nanotubes

The results of TG/DTG analysis of cement pastes modified by MWCNT in the dosage of 0–0.12% bwoc and cured for 28 days under normal conditions are listed in Table 3.5. Based on the results of the TG/ DTG analysis, the remarkable differences were not identified. The mass loss related with dehydration of cement hydration products and portlandite decomposition for nanomodified cement paste changed not significantly in comparison with reference sample without admixture.

Table 3.5. Results of thermal analysis

Sample	90–200 °C		430–465 °C		650–750 °C	
	Rel. mass change, wt%	Enthalpy, J/g	Rel. mass change, wt%	Enthalpy, J/g	Rel. mass change, wt%	Enthalpy, J/g
0% MWCNT	6.60	–200.96	–3.00	–158.13	1.69	–76.09
0.060% MWCNT	6.43	–199.62	–3.05	–165.43	1.52	–67.14
0.120% MWCNT	6.36	–197.30	–3.06	–178.21	1.40	–64.23

The FTIR spectroscopy was carried out to confirm the chemical interactions between components of nanomodified cement-based materials. The hardened cement paste with PCE and MWCNT suspension with PCE at the age of 7 days were prepared for FTIR spectroscopy. The results of FTIR spectroscopy are presented in Fig. 3.41.

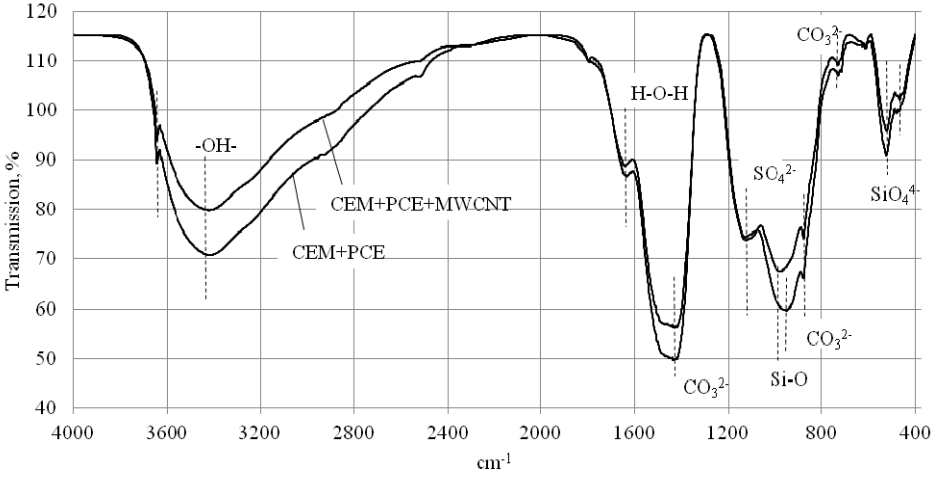


Fig. 3.41. Fourier-transform infrared spectroscopy for the modified cement-based materials

The following peaks were established:

- the peaks at 3645 cm^{-1} and 3419 cm^{-1} corresponds to the symmetric and asymmetric O–H stretching (ν1 and ν3) of $Ca(OH)_2$ (Shi *et al.* 2019; Trezza 2007);
- the band closer to 1650 cm^{-1} indicates the deformation mode H–O–H (ν2) of the molecular water absorbed (Trezza 2007);
- the peaks at 1435 cm^{-1}, 875 cm^{-1} and 729 cm^{-1} correspond to the vibrations of carbonate, CO_3^{2-} (Shi *et al.* 2019; Trezza 2007; Parveen *et al.* 2015);
- the peaks at approximately 1124 cm^{-1} and 1127 cm^{-1} are attributed to ν3 vibration of the SO_4^{2-} group in sulfates (Yang *et al.* 2017);
- the peaks at 950 cm^{-1} and 975 cm^{-1} for hardened cement pastes modified by MWCNT suspension with MWCNT and PCE, respectively, is caused by ν3 stretching of Si–O (Trezza 2007);
- the transmission peaks 465 cm^{-1} and 524 cm^{-1} correspond to out-of-plane bending vibration (ν4) and in-plane bending vibrations (ν2) which are linked with the polymerization of the silicate (SiO_4^{4-}) (Souza *et al.* 2020; Shi *et al.* 2019).

The modification of cement paste by MWCNT suspension and PCE does not cause the occurrence of new chemical bonds that confirms the absence of chemical interactions between MWCNT and cement hydration products. However, some changes were observed in the transmission intensity of peaks. The decrease of the peaks intensity at 3645 cm^{-1}, 3419 cm^{-1} and 1640 cm^{-1} can be caused by the retardation effects of the cement hydration process with formation of less amount of $Ca(OH)_2$. This retardation can be explained by the presence of CMC in MWCNT suspension that was observed in the calorimetric investigation (see section 3.3). The interactions between functional groups of CMC and PCE, the high surface area of MWCNT and its ability to absorb water can cause the changes in O–H vibrations of cement-based materials as well.

The lesser amount of $Ca(OH)_2$ leads to the decrease of formation of calcium carbonate during carbonation processes after reaction with CO_2 from the environment (see the decrease in intensity of the peaks at 1435 cm^{-1}, 875 cm^{-1} and 729 cm^{-1}). Besides, the retardation processes contribute to the changes in the formation of calcium hydrosilicates. The changes in calcium hydrosilicates are confirmed by the decrease in the peaks intensities at 975 cm^{-1}, 465 cm^{-1} and 524 cm^{-1}. The shift of the peak from 950 cm^{-1} to 975 cm^{-1} for cement paste with PCE and with MWCNT suspension and PCE, respectively, points out the changes in the cement hydration products. Not proportional increase in peak intensity at 1124 cm^{-1} for cement paste with MWCNT suspension and PCE can be linked with faster hydration reaction of tricalcium aluminate that is correlated with results of Rietveld phase analysis presented above.

3.4.2. The Influence of Nanotubes on Morphology of Cement Hydration Products

The SEM was performed to identify the effect of MWCNT on the morphology of cement hydration products. The prepared cement paste with W/C ratio of 0.5 was cured in the water at (20±1.0) °C for 3 days. SEM analysis was carried out on fractured surfaces of hardened cement paste reinforced by MWCNT.

SEM image in Fig. 3.42 presents the placement of MWCNT on the cement hydration products and in the pore volume. MWCNT do not react chemically with cement hydration products that is confirmed by their pure surface without any formations on them. The high ratio of MWCNT between diameter and length explains their ability to roll and form bundles on the surface of cement hydration products and in the pore volume. The formation of the cement hydration products is started on or around the MWCNT surface caused by the presence of MWCNT in mixing water before the beginning of the cement hydration process.

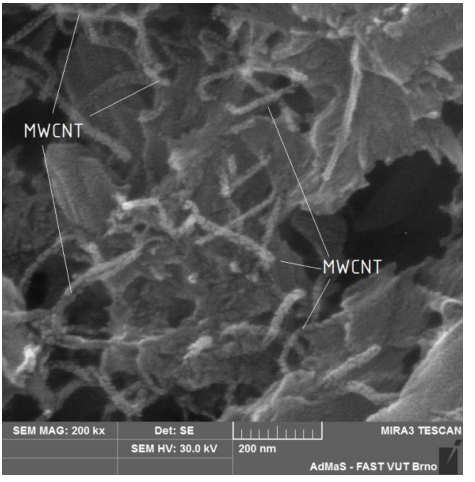
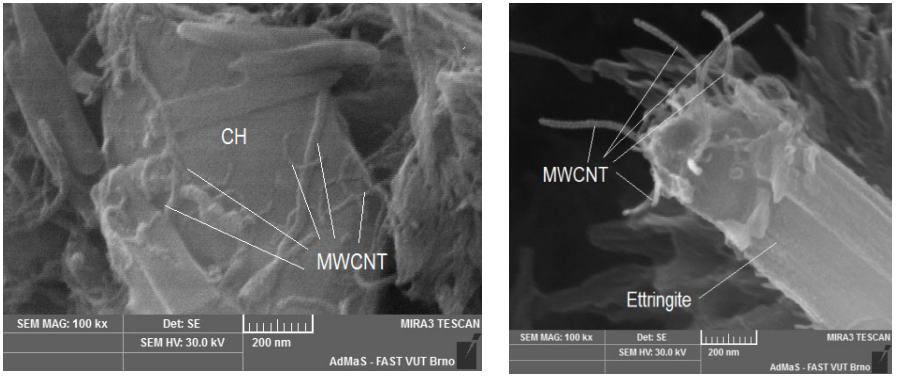


Fig. 3.42. Placement of nanotubes on the cement hydration products

Fig. 3.43 shows the placement of MWCNT on the surface CH and ettringite. The presence of MWCNT in the mixing water can change the crystallization processes in the cement matrix. The cement hydration products can be based on the surface of MWCNT and, as a consequence, change the behaviour of the crystallization process. MWCNT can act as crystallization centres for cement hydration products. At the same time, the high surface area of MWCNT and their po-

rous structure can hinder the part of mixing water with further retardation effects in the initial hydration process.



a) b)

Fig. 3.43. Placement of nanotubes: a) on the surface of CH and b) ettringite

MWCNT can act as a reinforcement of a cement matrix. Fig. 3.44 presents MWCNT in the capillary between two parts of C-S-H gel which bond them together. However, MWCNT can be pulled out under some external forces caused by the absence of chemical interactions and bonding between them and cement hydration products. The higher tensile strength of MWCNT (about 10 GPa) can be a reason for pull out effects in the cement matrix modified by MWCNT (Xu *et al.*, 2015).

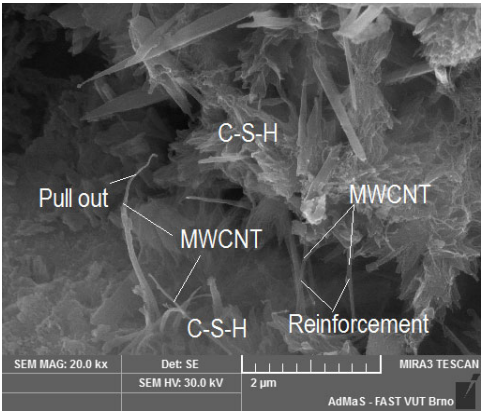


Fig. 3.44. Nanotubes in the capillary between two parts of agglomeraton of C-S-H

MWCNT occupy the pore volume between cement hydration products. The filling effect of MWCNT contributes to the densification of the cement matrix. Fig. 3.45 shows the placement of MWCNT in the pore volume between cement hydration products.

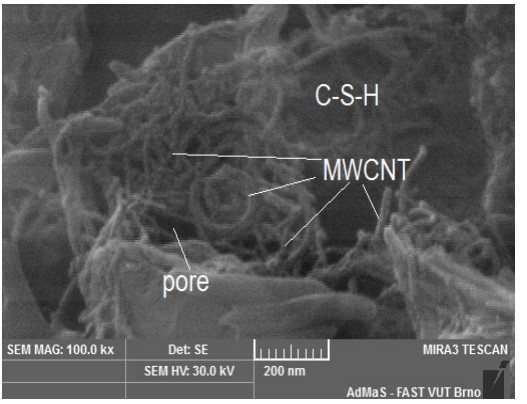


Fig. 3.45. Pores filling effect of nanotubes in hardened cement paste

SEM revealed the distribution of MWCNT on the cement hydration products and the absence of chemical interactions between them. MWCNT effect on the morphology of cement hydration products through their nucleating, reinforcement and filling effects. However, the ability of MWCNT to form bundles due to their high aspect ratio and pull out effects should be taken into account for prediction of properties of cement-based materials in a hardened state.

3.4.3. The Results of Microporosity of Hydrated Cement Pastes with Nanotubes

The nitrogen adsorption-desorption porosimetry (NADP) of nanomodified cement pastes at the age of 7 days and dried at the temperature of 60°C for 14 days before porosimetry revealed the following. The modification of cement paste by MWCNT in the dosage from 0 to 0.12% bwoc did not have a significant impact on the cement paste cumulative pore volume.

The cumulative pore volume was changed from 0.064 cc/g to 0.060 cc/g for the reference sample without MWCNT and sample modified by MWCNT in the dosage of 0.12% bwoc, respectively. The pore size distribution for tested samples is presented in Fig. 3.46–3.49.

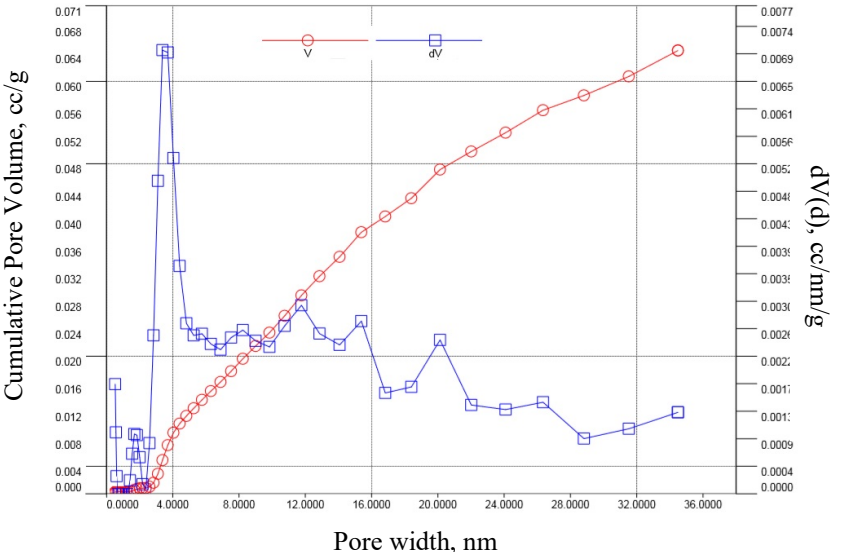


Fig. 3.46. Pore size distribution for the reference cement paste without of nanotubes at the age of 7 days

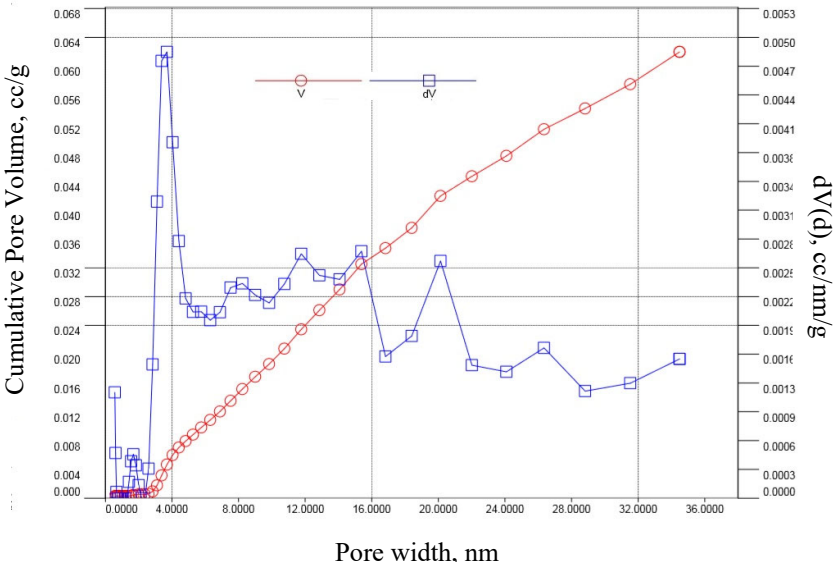


Fig. 3.47. Pore size distribution for the cement paste modified by 0.03% bwoc of nanotubes at the age of 7 days

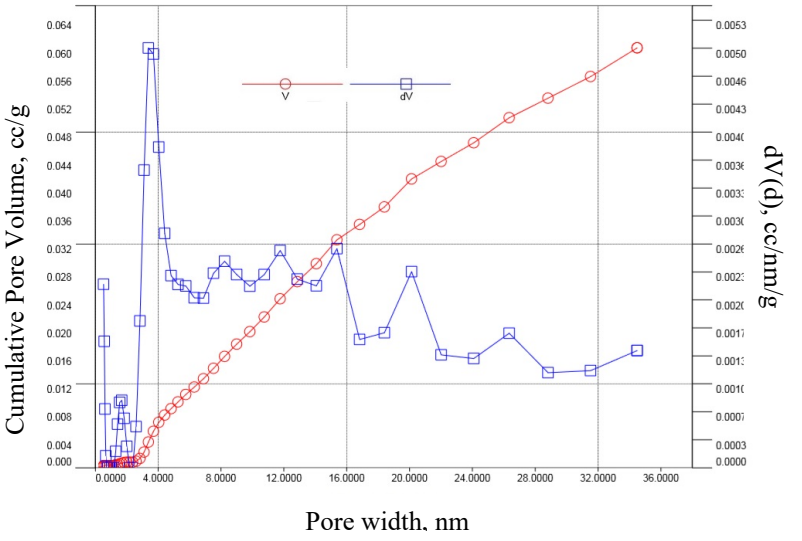


Fig. 3.48. Pore size distribution for the cement paste modified by 0.06% bwoc of nanotubes at the age of 7 days

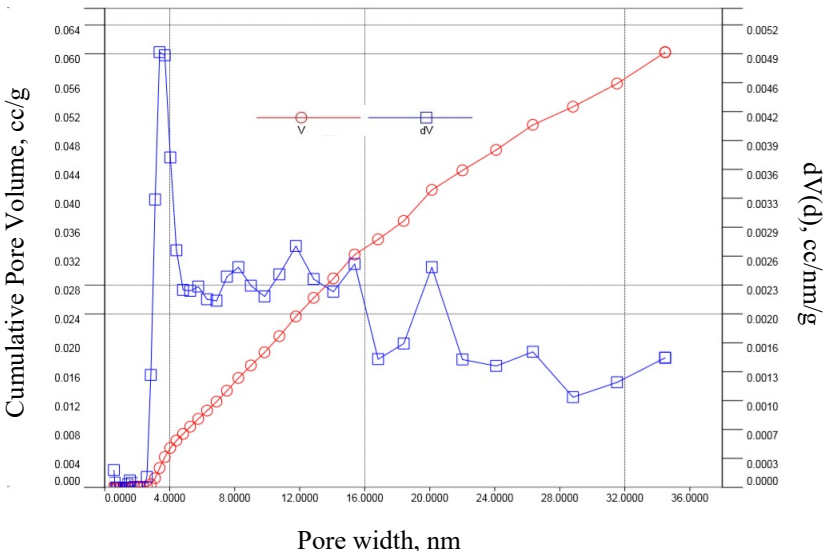


Fig. 3.49. Pore size distribution for the cement paste modified by 0.12% bwoc of nanotubes at the age of 7 days

Table 3.6. Results of porosimetry

Sample	0% MWCNT	0.03% MWCNT	0.06% MWCNT	0.12% MWCNT
Cumulative pore volume, cc/g	0.064	0.062	0.060	0.060
Surface area, m^2/g	15.363	12.947	13.495	11.670

The surface area of pores in hardened cement pastes with the addition of MWCNT in the dosage 0–0.12% bwoc decreased. The maximum decrease of surface area from 15.363 m^2/g (for reference sample) to 11.670 m^2/g was observed with an increase of MWCNT dosage up to 0.12% bwoc. Table 3.6 presents the results of porosimetry. These obtained results can be associated with the changes in hydration processes (see section 3.3) of nanomodified cement-based materials and the subsequent changes in the morphology of cement hydration products which specified by the performed XRD, thermal analysis and SEM in section 3.4.1, 3.4.2.

3.5. Conclusions of Chapter 3

1. The ultrasonication for 6 min with intensity of 400 W, 20 kHz with probe VS 200 T (Ø25mm, amplitude – 82 μm) is an optimal homogenization method for the obtaining of stable MWCNT suspension. The complex application of MWCNT and Pl led to the slight decrease of the average particle size of suspension up to 220 and 240 nm, respectively, in case of LS and NF. The average particle diameter was increased up to 470 nm in case of a modification of MWCNT suspension with PCE plasticizer due to intermolecular interaction between MWCNT with CMC and the carboxyl groups of PCE. The significant coagulation processes in homogenized MWCNT suspension was not observed for one month of the ageing process.
2. The cement pastes modified by MWCNT suspension without and with Pl characterized by different flow behaviour. The cement pastes without and with LS, NF possesses by shear thinning flow behaviour, with PCE by the shear thickening flow behaviour. MWCNT do not have a significant influence on the flow behaviour of cement paste. Mainly, the flow behaviour of cement paste was determined by the type of applied Pl. However, in the case of usage of PCE, the shear thickening effect decreased from MWCNT dosage of 0.03% bwoc.
3. The MWCNT suspension increases yield stress and plastic viscosity of cement pastes but in different extent depending on the type of Pl. More

remarkable changes in rheological parameters were observed for cement paste modified by MWCNT suspension with PCE. The increase in yield stress of cement paste by 265% was established with an increase in MWCNT dosage from 0 to 0.12% bwoc. The increase of MWCNT dosage from 0 to 0.12% led to the increase of plastic viscosity of cement paste by 107%. Other types of Pl did not increase yield stress and plastic viscosity remarkably (no more than 10–20%).

4. The test of the rheological parameters (yield stress and plastic viscosity) in 120 min time after cement paste mixing revealed the increase of them for cement paste modified by MWCNT without plasticizers and with LS and NF (up to 23%) As for cement paste modified by MWCNT suspension with PCE, yield stress and plastic viscosity were decreased up to 11% in 120 min after cement paste mixing.
5. Water bleeding of cement pastes reduced by 85%, 99%, 100% and 83%, respectively, in case of modification by MWCNT suspension without Pl, with LS, NF and PCE with an increase of MWCNT dosage up to 0.24% bwoc.
6. Considering the effect of CMC, MWCNT slightly accelerate the cement hydration processes. The usage of 0.12% MWCNT without plasticizing admixtures and with LS, NF and PCE led to the increase in the total heat emission by 21.6, 38.2, 62.2 and 30.8 J/g, respectively. However, the acceleration effect of MWCNT inhibits by the presence of carboxymethyl cellulose in the MWCNT suspension.
7. XRD, thermal analysis and FTIR spectroscopy of hardened cement paste with MWCNT did not identify the new phases in cement hydration products. Rietveld analysis showed an acceleration of C_3A and C_2S and retardation of C_3S hydration process in case of the modification of cement by MWCNT.
8. FTIR spectroscopy identified the increase of the peak intensity in the range 3200–3600 cm^{-1} that corresponds to the hydrogen bonds. The observed changes are associated with the interactions between MWCNT with CMC and functional groups of PCE which explain the increase in plastic viscosity of nanomodified cement paste and the prevention of the increase in plastic viscosity during the time after mixing.
9. MWCNT place on the surface of the cement hydration products, occupy the volume in the pores between cement hydration products and work as a reinforcement of cement matrix by MWCNT. The pure surfaces of MWCNT pointed out the absence of chemical interactions between MWCNT and cement hydration products.
10. Nitrogen adsorption-desorption porosimetry revealed the absence of the changes in cumulative pore volume with an increase of MWCNT dosage

from 0 to 0.12% bwoc. Whereas the surface area decreased by 24% with the addition of 0.12% MWCNT in comparison with the reference sample without admixture that can confirm the changes in hydration processes of nanomodified cement pastes.

General Conclusions

1. The UZ homogenization for 6 min with an intensity of 400 W and frequency of 20 kHz is obtained as an optimal MWCNT homogenization method, which enables to kept MWCNT suspension in suitable homogeneous conditions for one month period.
2. The shear thinning/ thickening rheological behaviour of mixtures is determined by the type of applied plasticizing admixture and is not depends on MWCNT dosage for cement pastes without plasticizing admixture and with LS and NF. In complex with PCE, MWCNT decrease the dilatancy of cement paste.
3. MWCNT with and without plasticizing admixture increase the yield stress and plastic viscosity of cement-based mixtures. In case of a modification of cement-based mixtures by MWCNT in the dosage up to 0.24% bwoc without plasticizing admixture and with LS and NF plasticizers, the increase in yield stress and plastic viscosity was up to 20% and did not have a significant influence on the effectiveness of this plasticizers. The complex modification of cement paste by MWCNT and PCE increases the yield stress and plastic viscosity and reduces the effectiveness of this plasticizer from the MWCNT dosage of 0.06% bwoc and 0.015% bwoc, respectively. The yield stress and plastic viscosity of

cement paste with PCE enhanced by 265% and 107% in MWCNT dosage of 0.12% bwoc due to the interactions between MWCNT with CMC and functional groups of PCE. These interactions were confirmed by FTIR spectroscopy which identified the increase in the peak intensity of hydrogen bonds vibrations in the range 3200–3600 cm^{-1}.

4. The yield stress and plastic viscosity of cement pastes modified by MWCNT without plasticizers and with LS and NF increased (up to 23%) in 120 min after cement paste mixing. The yield stress and plastic viscosity of the cement pastes modified by MWCNT suspension with PCE not remarkably decreased (up to 11%) in 120 min after cement paste mixing in MWCNT dosage over 0.03% bwoc.
5. Modification of cement paste by MWCNT suspension increases the stability of cement systems by the reduction of the volume coefficient of water bleeding by 85%, 99%, 100% and 83%, respectively, for MWCNT suspension without plasticizing admixtures, with LS, NF and PCE with an increase of MWCNT dosage up to 0.24% bwoc.
6. Considering the impact of CMC in MWCNT suspension, MWCNT with and without plasticizing admixtures slightly accelerate the cement hydration processes and increase total heat emission. MWCNT in the dosage of 0.12% separately and in combination with LS, NF and PCE increase the total heat emission by 21.6, 38.2, 62.2 and 30.8 J/g after 48 h of hydration.
7. X-ray diffraction, simultaneous thermal analysis and FTIR spectroscopy of MWCNT modified cement paste did not identify the new phases in cement hydration products. The quantitative Rietveld phase analysis revealed that modification of cement-based materials by MWCNT accelerates C_3A and C_2S and retards C_3S hydration process during Portland cement hydration.
8. MWCNT change the cement hydration process and morphology of cement hydration products. MWCNT do not have chemical interactions with cement hydration products, remain their smooth surface, distribute close to surfaces of cement hydration products and form bundles in pore volume. Increase of MWCNT dosage from 0 to 0.12% bwoc did not have an effect on cumulative pore volume of hardened cement paste and decrease the surface area by 24% due to the increase in pore sizes that can be associated with changes in cement hydration processes and morphology of hydration products.

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Summary in Lithuanian

Įvadas

Problemos formulavimas

Tobulėjant nanotechnologijoms, kiekvienais metais vis didėja anglies nanovamzdelių (ANV), įskaitant daugiasluoksnių anglies nanovamzdelių (DSANV) panaudojimo betono modifikavimui susidomėjimas. Dėl išskirtinių savybių ANV gali būti naudojami kaip sudėtinių betono priedų komponentas. Nepaisant didelio tyrimų kiekioto, ANV pritaikymas cementinių kompozitų modifikavimui statybų technologijoje praktikoje yra ribotas dėl nesistemingų ir nestabilių rezultatų. Pagrindinė ANV panaudojimo problema yra susijusi su jų gebėjimu koaguliuoti dėl milžiniško savitojo paviršiaus ploto ir stiprių Van der Waalso jėgų tarp dalelių. Racionalių ANV homogenizavimo metodų, optimalių paruoštos suspensijos kontrolės metodų, cemento tešlų su ANV priedu reologijos, hidratacijos ir sukietėjusio cementinio akmens susidarymo supratimo paieškoms reikalingi papildomi tyrimai.

Darbo aktualumas

Betono gamyboje plastifikuojančios įmaišos (Pl) vis plačiau naudojamos reologinių ir technologinių savybių, cemento hidratacijos proceso ir sukietėjusio cementinio akmens mikrostruktūros pagerinimui. ANV dėl unikalių smulkumo bei fizinių ir mechaninių savybių kartu naudojami su Pl gali turėti įtakos mišinių plastifikavimo efektyvumui, reologinei elgesenai ir stabilumui, ir dėl to pagerinti cementinių sistemų savybes skysto-

je ir sukietėjusioje būsenoje po cemento hidratacijos proceso. Nepaisant didelio tyrimų skaičiaus, ANV ir skirtingų tipų Pl sąveikos mechanizmai cementiniuose mišiniuose nėra visiškai išaiškinti ir reikalauja tolesnio tyrimo.

Tyrimo objektas

Tyrimo objektas yra cemento pagrindu pagamintos medžiagos, modifikuotos DSANV suspensija su plastifikuojančiomis įmaišomis skystoje ir sukietėjusioje būsenoje.

Darbo tikslas

Tyrimo tikslas – nustatyti DSANV ir plastifikuojančių įmaišų sąveikos mechanizmą, vertinant jų poveikį cementinių mišinių reologinėms savybėms, cemento hidratacijos procesui ir sukietėjusio cementinio akmens mikrostruktūrai.

Darbo uždaviniai

Siekiant disertacijos tikslo, suformuluoti šie darbo uždaviniai:

1. Sukurti suspensijos homogenizavimo metodiką priklausomai nuo DSANV kiekio ir Pl tipo, parinkti optimalų suspensijos homogenizavimo metodo tipą ir intensyvumą. Įvertinti DSANV suspensijos savybes po homogenizacijos ir nustatyti DSANV suspensijos elgseną senėjimo metu.
2. Įvertinti reologines cemento tešlų, modifikuotų DSANV suspensija kartu su skirtingais Pl tipais ir be jų, savybes. Nustatyti DSANV suspensijos kiekius, turinčius įtakos mišinių ribiniams šlyties įtempiams, plastiniam klampiui ir tiksotropiškumo/ dilatantiškumo rodikliui.
3. Ištirti DSANV suspensijos įtaką cemento tešlų stabilumui su skirtingomis plastifikuojančiomis įmaišomis ir be jų.
4. Ištirti DSANV suspensijos poveikį cemento tešlos hidratacijos kinetikai, sukietėjusio cementinio akmens mineralinei sudėčiai ir mikrostruktūrai kartu su skirtingomis plastifikuojančiomis įmaišomis ir be jų.

Tyrimų metodika

Tyrimuose naudotos DSANV suspensijos homogenizavimo ir apibūdinimo, modifikuotos cemento tešlos reologinių charakteristikų nustatymo ir modifikuotų cemento kompozitų mikrostruktūros bandymų metodikos.

DSANV suspensijos homogenizavimui naudotas zondo tipo ultragarsinis poveikis. Paruoštos DSANV suspensijos apibūdinimui buvo naudojami pH, elektrinio laidumo, zeta potencialo, paviršiaus įtempio, dalelių dydžio matavimai ir FTIR spektoskoskopija.

Reologinių parametrų tyrimai atlikti rotaciniu reometru su koaksialiniais cilindrais skirtingu laiku po cemento tešlos sumaišymo, naudojant specialiai parinktą šlyties greičio režimą. Eksperimentiniai reologinių matavimų duomenys buvo apdoroti pagal Herschel-Bulkley modelį.

Cemento tešlų hidratacijos procesas buvo tiriamas izoterminiu kalorimetru. Sukietėjusios cemento tešlos mikrostruktūra ir hidratacijos produktų morfologija buvo tiriama XRD, terminės analizės, azoto porometrijos, SEM ir FTIR spektroskopijos metodais.

Mokslinis naujumas

Disertacijos tyrimų metu gauti nauji medžiagų inžinerijos mokslo rezultatai:

1. Nustatytas DSANV ir skirtingos genezės plastifikuojančių įmaišų kompleksinio poveikio cementiniuose mišiniuose mechanizmas.
2. Nustatyti DSANV kiekiai, darantys įtaką plastifikuotų, ir neplastifikuotų cemento tešlų reologiniams parametrams (ribiniams šlyties įtempiams, plastiniam klampiui, tiksotropiškumo/dilatantiškumo rodikliui) ir jų vandens atsiskyrimui.
3. Nustatyti cemento mišinių, modifikuotų DSANV suspensija su įvairių tipų plastifikuojančiomis įmaišomis, hidratacijos proceso parametrai.

Darbo rezultatų praktinė reikšmė

Tyrimų rezultatus galima panaudoti kuriant kompleksines įmaišas su DSANV ir plastifikliais cementiniams mišiniams (skiediniams, betonams ir kitiems). Cementinių medžiagų tekamumo parametrų ir hidratacijos proceso valdymas modifikuojant kompleksinėmis įmaišomis gali būti pritaikytas betono transportavimo, klojimo, pumpavimo siurbliais ir sutankinimo technologijoms tobulinti. Be to, kompleksinės įmaišos su DSANV gali užtikrinti betono mišinių be vandens atsiskyrimo, reikalingų įvairiam techniniam pritaikymui, pavyzdžiui didelio klojumo betonams, savaime sutankėjantiems betonams ir betono mišiniams 3D spausdinimui, gamybą.

Ginamieji teiginiai

1. Dėl didelio dalelių smulkumo ir paviršiaus ploto DSANV kartu su įvairiais Pl keičia šių cheminių įmaišų plastifikavimo efektyvumą ir sumažina vandens atsiskyrimą iš cementinių mišinių.
2. DSANV priedas pagreitina plastifikuotų cemento mišinių hidratacijos procesus dėl savo fizinio poveikio, tokio kaip tarpmolekulinis, elekrokinetinis ir kiti.
3. DSANV nesukelia naujų produktų susidarymo cemento hidratacijos metu dėl savo cheminio inertiškumo. DSANV keičia cementinės matricos morfologiją dėl fizinės sąveikos su cemento hidratacijos produktais.

Darbo rezultatų aprobavimas

Autorė paskelbė 12 mokslinių straipsnių disertacijos tema: du – moksliniuose žurnaluose, įtrauktuose į „Clarivate Analytics Web of Science“ duomenų bazės leidinius, turinčius citavimo indeksą (Skripkiunas ir kt., 2018; Skripkiunas ir kt., 2019) ir vieną be citavimo indekso (Skripkiunas et al. 2019), keturis straipsnius kitų duomenų bazių leidiniuose (Karpova et al., 2014; Karpova et al., 2015; Skripkiunas et al., 2017; Karpova ir kt., 2019 m.), tris straipsnius konferencijų pranešimų medžiagoje, įtrauktoje į „Clari-

vate Analytics Web of Science“ duomenų bazę (Yakovlev ir kt., 2019; Skripkiunas ir kt., 2019a; Skripkiunas ir kt., 2019b), du straipsnius kitų duomenų bazių konferencijų pranešimų medžiagoje (Skripkiunas ir kt., 2018a; Skripkiunas ir kt., 2018b). Doktorantūros studijų laikotarpiu (2016–2020 m.) autorė skaitė 12 pranešimų mokslinėse konferencijose, 10 iš jų tarptautinėse.

Disertacijos struktūra

Disertaciją sudaro įvadas, trys skyriai, bendrosios išvados, literatūros šaltinių sąrašas (159 publikacijos), autoriaus publikacijų mokslinių tyrimų tema sąrašas (12 publikacijų), santrauka lietuvių kalba ir 7 priedai. Disertacijos apimtis (be priedų) yra 142 puslapiai. Tekste yra 3 numeruotos formulės, 13 lentelių ir 70 paveikslų.

1. Plastifikuojančių įmaišų ir nanovamzdelių poveikis cementinių mišinių savybėms

ANV poveikio cementinių mišinių technologinėms savybėms tyrimų skaičius nuolat auga. Konsta-Gdoutos *ir kt.* (2017), Collins *ir kt.* (2012) nustatė cementinių mišinių tekamumo pablogėjimą. Priešingai nei šių mokslininkų, cemento sistemų su DSANVir paviršių aktyvinančia medžiaga bandymai neparodė reikšmingų mišinių technologinių savybių pokyčių.

Daugelis tyrimų rodo, kad cementinių mišinių modifikavimas DSANV pagerina sukietėjusių mišinių mechanines savybes. Tačiau DSANV poveikis cementiniams kompozitams skirtingomis sąlygomis nėra vienodas. Xu *ir kt.* (2015), Carrico *ir kt.* (2018) nustatytas cementinių nišinių gniuždymo stiprio padidėjimas atitinkamai 15 % ir 21 %. Lenkimo stiprio pokyčių vertės taip pat nėra stabilios skirtinguose tyrimuose.Al-Rub *ir kt.* (2012) gavo cementinių medžiagų lenkimo stiprio padidėjimą 269 %, o Rocha *ir kt.* (2019) gavo 46 % padidėjimą.

Dauguma tyrimų rodo mikrostruktūros pokyčius cemento kompozituose, modifikuotuose DSANV – bendro poringumo sumažėjimą ir porų dydžio pasiskirstymo pagerėjimą (Xu *ir kt.* 2015; Al-Rub *ir kt.* 2012; Han *ir kt.* 2015; Melo *ir kt.* 2011; C*ui ir kt.* 2017; Yakovlev *ir kt.* 2017 m.). Alafogianni *ir kt*. (2019) nustatytė, kad nedideli ANV kiekiai iki 0,4 % cemento masės sumažina cemento skiedinio įgėrį iki 50 % dėl tobulesnio porų pasiskirstymo skiedinyje.

Skirtingi požiūriai egzistuoja dėl cementinių mišinių su nanovamzdeliais hidratacijos kinetikos. Nadiv *ir kt.* (2016), Cui *ir kt.* (2015), Guan *ir kt.* (2020), Alatawna *ir kt.* (2020), Li *ir kt.* (2019) pastebėjo cemento hidratacijos reakcijos pagreitėjimą cementiniuose mišiniuose su ANV. Priešingas ANV poveikis cemento hidratacijos kinetikai aprašytas Isfahani *ir kt.* (2016), Leonavičius *ir kt.* (2018), Amin *ir kt.* (2015), Tafesse *ir kt.* (2019). Isfahani *ir kt*. (2016), kurie nustatė cemento hidratacijos lėtėjimą ir hidratacinės šilumos sumažėjimą 43,4 %, o tai buvo paaiškinta ANV aglomeracija aplink cemento daleles, kuri trukdo cemento hidratacijai.

Apibendrinant anksčiau atliktų tyrimų rezultatus, galima daryti išvadą, kad ANV poveikis cementiniams mišiniams dėl daugelio veiksnių nėra stabilus ir reikalauja tolesnio tyrimo. Šis tyrimas skirtas DSANV suspensijos kartu su plastifikuojančiomis įmai-

šomis poveikiui cementinių mišinių reologinėms savybėms, cemento hidratacijos procesui ir sukietėjusios cementinio akmens mikrostruktūrai nustatyti.

2. Nanomodifikuotų cementinių mišinių tyrimams naudotos medžiagos ir tyrimo metodai

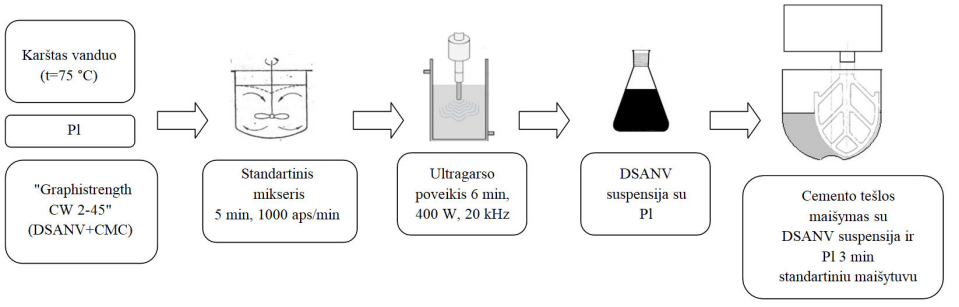
Eksperimentiniams tyrimams buvo naudojamas Portlandcementis be mineralinių priedų CEM I 42,5 R, atitinkantis EN 197-1. LS, NF ir PCE įmaišos buvo naudojamos kaip plastifikuojančios cementinius mišinius.

DSANV suspensija buvo gaminama iš „Graphistrength CW 2-45“ granulių su anglies nanovamzdeliais, pagamintų bendrovės „Arkema“ (Prancūzija). Anglies nanovamzdelių granulėse yra 45 % DSANV ir 55 % karboksilmetil celiuliozės (CMC) pagal masę. DSANV ilgis 0,1–10 μm, o skersmuo – 15–20 nm.

Ruošiant DSANV suspensiją granulės „Graphistrength CW 2-45“ buvo panardintos į karštą vandenį, kurio temperatūra yra apie 75 °C, ir maišomos mikseriu apie 1000 aps./min, maišymo trukmė 5 min. Po to suspensija buvo apdorojama ultragarsu strypinio zondo tipo įrenginyje 20 kHz, 400 W, ultragarsinio apdorojimo trukmė 6 min. Buvo ruošiama 200 ml suspensijos.

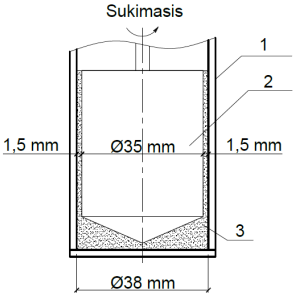
Po homogenizacijos DSANV suspensijoms buvo tiriamas pH, elektrininis laidumas, zeta potencialas, dalelių dydis, paviršiaus įtempiai ir atliekama FTIR spektroskopija. Kai kurios DSANV suspensijos savybės buvo bandomos ir po 1 mėnesio, kad būtų galima įvertinti suspensijos stabilumą sandėliavimo laikotarpiu.

Cemento tešlos paruošimui buvo naudojama 200 g cemento kiekvienam reologiniam bandymui. DSANV suspensijos buvo naudojamos kaip cemento tešlos modifikatorius kartu su vandeniu. DSANV dozė svyravo nuo 0 iki 0,24 % cemento masės. LS, NF ir PCE plastifikuojančių įmaišų dozė buvo 1 % cemento masės visoms cemento tešloms. Cemento tešlos modifikavimo schema DSANV suspensija su ir be Pl pavaizduota S2.1 paveiksle.



S2.1 pav. Cemento tešlos modifikavimas daugiasluoksniais anglies nanovamzdeliais ir plastifikuojančios įmaišos

Cementinių mišinių reologijos bandymas buvo atliekamas rotaciniu reometru Rheotest RN 4.1 (S2.2 pav.) su koaksialiniais cilindrais pagal šlyties greičio mažinimo nuo 100 s^{-1} iki 0,1 s^{-1} režimą pakopomis po 5, 60, 120 min po cemento tešlos sumaišymo. Pagrindiniai reologiniai parametrai, tokie kaip ribiniai šlyties įtempiai τ_0 ir plastinis klampis μ, buvo nustatyti iš mišinio tekėjimo kreivės (diagrama tarp šlyties įtempių τ ir šlyties greičio γ intervale nuo 0,1 iki 100 s^{-1}), naudojant Herschel-Bulkley reologinį modelį.



S2.2 pav. Mišinių bandymo rotaciniame reometre Rheotest RN 4.1 su koaksialiniais cilindais chema: 1– nejudantis cilindrinis indas, 2 – judantis cilindras, 3 – cemento tešla

Atsiskyrusio vandens kiekis buvo nustatytas pagal tokią metodiką: 50 g DSANV suspensijos, paruoštos pagal anksčiau aprašytą metodiką, buvo supilama į 200 ml plastikinį indą. Po to 50 g cemento buvo įmaišoma per 1 min ir DSANV suspensijos ir cemento mišinys buvo nuolat maišomas 4 min. Plastikinis indas paliekamas stovėti nejudant. Po 2 valandų nuo sumaišymo švirkšto pagalba buvo surinktas atsiskyręs vanduo cemento tešlos paviršiuje. DSANV kiekis mišiniuose buvo keičiamas nuo 0 iki 0.24 % cemento masės, Pl kiekies mišiniuose su plastifikuojančiu priedu buvo 1 % cemento masės

Kalorimetrijos tyrimai buvo atlikti naudojant izoterminiu kalorimetru TAM AIR III. Visų bandinių V/C santykis buvo 0,50, Pl kiekies visuose bandiniuose buvo lygus 1 % cemento masės. DSANV dozė buvo keičiama nuo 0 iki 0,12 % cemento masės. Modifikuotų cemento tešlų rišimosi terminai nustatyti naudojant Viko prietaisą pagal EN 480-2, esant V/C santykiui 0,30 ir DSANV kiekiui 0,06 % cemento masės.

Modifikuoto cementinio akmens mikrostruktūra buvo ištirta naudojant rentgeno difrakcijos analizę (XRD), kombinuotą šiluminę analizę (STA) ir skenuojančią elektroninę mikroskopiją (SEM).

Medžiagų fazinės sudėties rentgeno difrakcijos (XRD) analizė buvo atlikta taikant difraktometrą DRON-7. Norint gauti rentgeno spinduliuotės Cu Ka spektrą (λ = 0,1541837 nm), buvo naudojamas grafito monochromatorius. Bandymų parametrai buvo tokie: įtampa – 30 kV; srovė – 12 mA; difrakcijos kampo diapazonas – nuo 4 iki 80°, detektoriaus judėjimo žingsnis – 0,02°; intensyvumo matavimo trukmė pakopoje – 0,5 s.

Siekiant atlikti kiekybinę XRD gautų duomenų analizę, buvo atlikta Rietveld fazinė analizė. Cemento mėginių kiekybinė Rietveld fazinė analizė buvo atlikta naudojant grafiniu pagrindu veikiančią profilio analizės programą (“TOPAS”) ir etalonų duomenis, paimtus iš PDF4 duomenų bazės.

Kombinuota šiluminė analizė (STA) buvo atliekama matuojant produktų fazinį transformavimą esant 10 °C/min temperatūros kėlimo greičiui, temperatūra buvo keliama nuo 30 iki 1000 °C azoto atmosferoje, mėginio masė buvo 15 mg. Bandymas buvo atliktas Linseis STA PT-1000 (Vokietija) instrumentu.

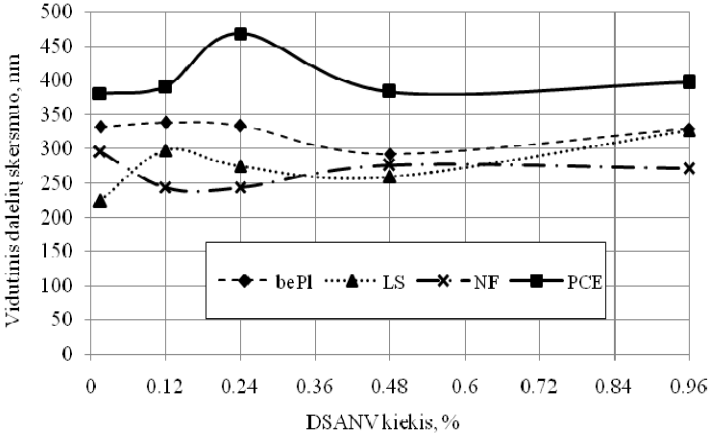
DSANV suspensijos, PCE bei 7 paras kietėjusio cementinio akmens FTIR spektrai buvo fiksuojami naudojant spektrofotometrą SPECTRUM GX 2000. Duomenys buvo registruojami spektriniame diapazone nuo 400 iki 4000 cm^{-1}.

Skenuojanti elektroninė mikroskopija (SEM) atlikta elektoniniu mikroskopu MIRA 3 Tescan, naudojant tokius parametrus: įtampa 30 kV, atstumas iki mėginio paviršiaus – nuo 7 iki 10 mm. Buvo tiriamas skeltas cementinio akmens arba išdžiovinto bandinio paviršius. Prieš bandymą bandinio paviršius buvo padengtas plonu aukso sluoksniu, taikant vakuuminio garinimo metodą.

Nanomodifikuoto cementinio kompozito mikroporingumo tyrimai buvo atlikti azoto adsorbcijos – desorbcijos porometrijos metodu, naudojant „Quantachrome Autosorb-iQ-KR / MP“ automatinį dujų sorbcijos analizatorių. Cementinio akmens bandiniai po 7 parų kietėjmo buvo džiovinami krosnyje 60 ° C temperatūroje 14 parų prieš poringumo bandymą. Porų paviršiaus plotas buvo apskaičiuotas naudojant BET (Brunauer – Emmett – Teller) lygtį. Visi skaičiavimai atlikti naudojant „Quantachrome Instrument“ „ASiQwin“ (2.0 versija).

3. Cementinių mišinių su daugiasluoksnių anglies nanovamzdelių ir plastifikuojančiomis įmaišomis struktūra ir savybės

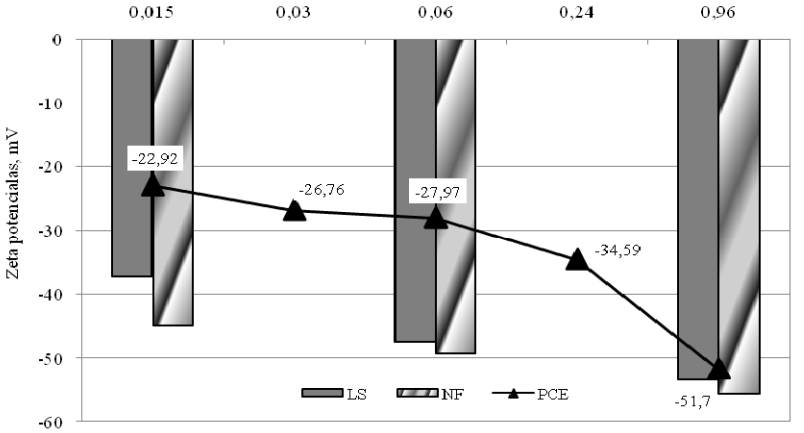
Tiriant DSANV suspensijos homogeniškumą, dalelių dydžio analizė atskleidė skirtingą Pl poveikį vidutiniam dalelių dydžiui. Kaip matyti iš S3.1 paveikslo, LS ir NF šiek tiek sumažina vidutinį dalelių dydį suspensijoje, palyginti su DSANV suspensija be Pl ir su PCE.



S3.1 pav. Daugiasluoksnių anglies nanovamzdelių suspensijos dalelių dydžio analizė

Mažiausi 224 nm ir 244 nm dalelių skersmenys buvo gauti DSANV suspensijai su LS ir NF. Priešingai nei LS ir NF poveikis, vidutinis dalelių dydis DSANV suspensijoje su PCE yra didesnis dėl PCE cheminės struktūros ir zeta potencialo, kuris yra mažesnis nei DSANV suspensijos su LS ir NF (S3.2 pav.). Vidutinio dalelių dydžio padidėjimas iki 468 nm buvo gautas DSANV suspensijoje su PCE dėl plastifklio karboksilo grupės galimų intramolekulinių ir tarpmolekulinių vandenilinių jungčių susidarymo.

LS, NF ir PCE sukelia skirtingus zeta potencialo pokyčius DSANV suspensijoje (S3.2 pav.). Padidėjus DSANV kiekiui suspensijoje su skirtingais Pl, zeta potencialas (neigiamas) padidėja atitinkamai 30 %, 19 % ir 56 % su LS, NF ir PCE plastifikuojančiomis įmaišomis atitinkamai. Didesnį zeta potencialo pokytį sukelia PCE. Zeta potencialo pokyčiai DSANV suspensijoje su skirtingos kilmės Pl susiję su jų pH verčių skirtumais.



S3.2 pav. Daugiasluoksnių anglies nanovamzdelių suspensijų zeta potencialas

DSANV suspensija pasižymi dideliu dispersiškumu ir laikui bėgantjai būdinga smulkių dalelių koaguliacija. DSANV suspensija su PCE buvo išbandyta po 1 mėnesio saugojimo laboratorinėse sąlygose. DSANV suspensijos pH vertė, kai DSANV koncentracija suspensijoje buvo 0,96 %, sumažėjo nuo 5,0 iki 4,7 po 1 mėnesio išlaikymo, o jos elektrinis laidumas išlaikymo metu padidėjo labai nežymiai.

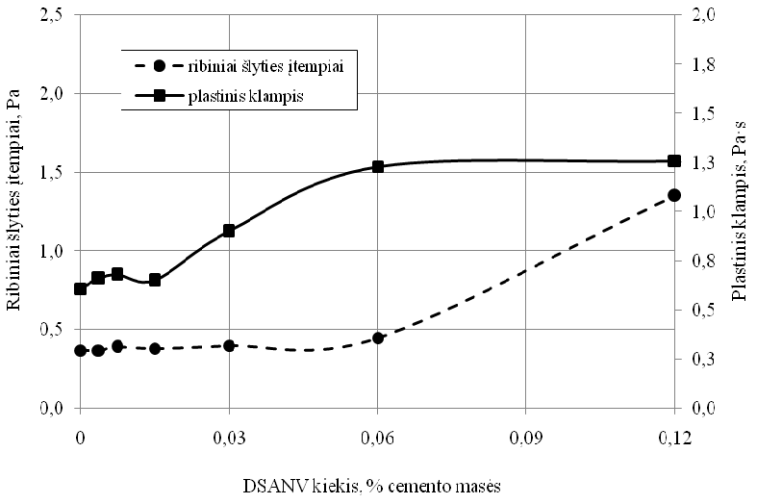
DSANV suspensijos dalelių dydžio analizė po pakartotinės homogenizacijos parodė, kad DSANV suspensijoje su PCE dalelių skersmuo svyravo nuo 150 iki 600 nm, o vidutinis dalelių skersmuo buvo lygus 376 nm. DSANV suspensijos su PCE bandymas po 1 mėnesio saugojimo parodė dalelių dydžių svyravimą nuo 350 iki 900 nm ir vidutinį skersmenį 515 nm, o tai rodo dalelių aglomeracijos procesus DSANV suspensijoje.

Vienas iš veiksnių, lemiančių cementinių mišinių reologines savybes, yra jų dalelių dydis. Cemento dalelių dydis yra nuo 1 iki 80 μm, o vidutinė cemento dalelių dydžio vertė yra apie 14 μm. Pagrindinis dalelių kiekis DSANV suspensijoje yra 0,1–1 μm diapazone, o vidutinis nanodalelių skersmuo 293 nm (0, 293 μm). Tai rodo, kad cemento

dalelės yra apie 50 kartų didesnės už DSANV suspensijoje esančias daleles. Toks dalelių dydžio skirtumas turi vieną iš lemiamų vaidmenų keičiantis cemento tešlų su DSANV reologiniams parametrams.

FTIR spektroskopijos tyrimai rodo, kad DSANV suspensijos homogenizavimas kartu su PCE lemia šiuos pokyčius. Suspencijoje su DSANV smailės 3200–3600 cm^{-1} diapazone intensyvumas padidėja palyginus su suspencija tik su PCE. Šiuos pokyčius galima paaiškinti vandenilinių jungčių susidarymu tarp PCE ir CMC, kuris naudojamas kaip dispersinis agentas DSANV suspensijoje, funkcinių grupių. Vandenilinių jungčių susidarymas tarp DSANV su CMC ir PCE paaiškina cementinės tešlos plastinio klampio padidėjimą ir plastinio klampio vertės stabilumą laike po tešlos sumaišymo.

Reologinis cemento tešlos, modifikuotos DSANV suspensija su Pl ir be jų, bandymas, parodė, kad cemento tešlų ribiniai šlyties įtempiai ir plastinis klampis padidėjo atitinkamai 17 % ir 6 %, kai DSANV kiekis buvo padidintas iki 0,24 % cemento masės.



S3.3 pav. Cemento tešlos, modifikuotos daugiasluoksnių anglies nanovamzdelių suspensija ir polikarboksilato eteriu , ribiniai šlyties įtempiai ir plastinė klampa po 5 min po sumaišymo

Cemento tešlos, modifikuotos atskirai CMC 0,29 % bwoc kiekiu, reologiniai parametrai papildomai nustatyti norint išsiaiškinti CMC, esančios DSANV suspensijoje kaip disperguojančios medžiagos, įtaką. CMC suspensijos ribiniai šlyties įtempiai ir plastinis klampis buvo 3,2 Pa ir 2,65 Pa·s po 5 min po cemento tešlos sumaišymo. Šie parametrai yra panašūs, net šiek tiek mažesni už cenento tešlos be priedų parametrus. Tuo tarpu DSANV modifikuotos suspensijos, kurioje DSANV kiekis lygus 0,24 % cemento masės analogiški parametrai žymiai didesni ir lygūs 4,1 Pa ir 4,17 Pa·s. Tai rodo, kad DSANV lemia papildomą cemento tešlos ribinių šlyties įtempių ir plastinio klampio padidėjimą.

DSANV suspensija kartu su LS nežymiai padidina nanomodifikuotos cemento tešlos ribinius šlyties įtempius ir plastinį klampį atitinkamai 11 % ir 9 %. Pridėjus NF į DSANV suspensiją, ribiniai šlyties įtempiai padidėja 13 %, kai DSANV kiekis lygus 0,24 %. Cemento tešlos, modifikuotos DSANV suspensija su NF, plastinis klampis sumažėja 13 %, kai DSANV kiekis didinamas nuo 0 iki 0,12 %, ir pasiekia etaloninio bandinio (modifikuoto tik NF) vertę, kai DSANV kiekies lygus 0,24 % cemento masės.

Reikšmingesni cemento tešlos reologinių parametrų pokyčiai buvo nustatyti modifikuojant DSANV suspensiją PCE plastifikuojančiu priedu (S3.3 pav.). Padidinus DSANV kiekį iki 0,12 % cemento masės, cemento tešlos ribiniai šlyties įtempiai padidėja 265%, o plastinis klampis 107%.

Cemento tešla be Pl ir su LS ir NF pasižymi tiksotropiška reologine elgsena. Modifikuojant cemento tešlą DSANV kartu su LS ir NF, tiksotropiškumo rodiklis šiek tiek sumažėja atitinkamai nuo 0,70 iki 0,64 ir nuo 0,83 iki 0,72, įvedant DSANV iki 0,06 % cemento masės. Priešingai LS and NF, cemento tešlos modifikavimas PCE sukelia cemento tešlos dilatantišką reologinę elgseną. Padidinus DSANV kiekį nuo 0 iki 0,24 % cemento masės, cemento tešlos su DSANV ir PCE dilatantiškumo rodiklis beveik nekinta (sumažėja nuo 1,20 iki 1,17). Tyrimai rodo, kad DSANV kiekio cemento tešloje padidinimas iki 0,06 % cemento masės su visomis plastifikuojančiomis įmaišomis ir be jų nekeičia cementinės tešlos reologinės elgsenos (tiksotropiškumo/ dilatantiškumo).

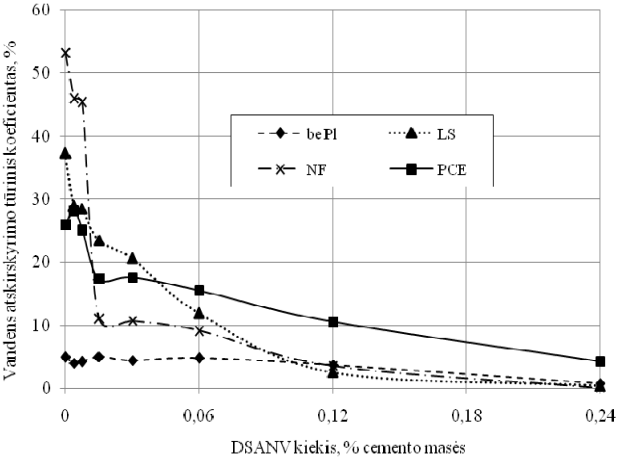
Nanomodifikuotos cemento tešlos tiksotropiškumo/ dilatantiškumo rodiklis reikšmingai nekinta per 120 min po cemento tešlos sumaišymo. Nanomodifikuotos cemento tešlos be Pl ir su LS, NF ribiniai šlyties įtempiai ir plastinis klampis per 120 min po cemento tešlos sumaišymo didinant DSANV kiekį iki 0,24 % cemento masės ribiniai šlyties įtempiai nežymiai padidėja atitinkamai 10 %, 4 %, 20 %. Cemento tešlos, modifikuotos DSANV suspensija ir PCE, per 120 min po cemento tešlos sumaišymo ribiniai šlyties įtempiai sumažėja 11 %, kai DSANV kiekis lygus 0,12 % cemento masės.

Cemento tešlos plastinis klampis, padidinus DSANV kiekį iki 0,24 %, padidėja atitinkamai 8 %, 21 %, 23 %, modifikuojant DSANV suspensija be Pl, su LS ir NF per 120 min po cemento tešlos sumaišymo. Plastinis klampis per 120 min po cemento tešlos sumaišymo sumažėja 8 % cemento tešlą modifikuojant DSANV suspensija su PCE. Tyrimų rezultatai rodo, kad cemento tešlos modifikavimas DSANV pailgina PCE plastifikavimo efektą cementiniuose mišiniuose.

Be reologinių tyrimų buvo nustatytas cemento tešlų, modifikuotų DSANV suspensija be ir su skirtingais Pl tipais, vandens atsiskyrimas. Kaip matyti iš S3.4 paveikslo, DSANV kiekio padidinimas cemento tešlose su visais Pl žymiai sumažina vandens atsiskyrimą iš cementinio mišinio.

Cemento tešloje be Pl dėl standžios tešlos konsistensijos vandens atsiskyrimas nedidelis ir nesikeičia iki DSANV kiekio 0,12 % cemento masės bei sumažėja viršijus ją iki 0,24 % cemento masės kiekio. Vandens atsiskyrimo (tūrio) sumažėjimas šiuo atveju lygus 85 % lyginant su etaloniniu bandiniu be DSANV modifikacijos. Pridėjus Pl į cemento tešlą, tešla tampa daug plastiškesnė ir padidėja tešlos vandens atsiskyrimas palyginus su cemento tešla be Pl. Vandens atsiskyrimo koeficientas cemento tešlose su LS, NF ir PCE žymiai sumažėja pridedant DSANV iki 0,03 % cemento masės ir palaipsniui mažėja viršijus šį kiekį iki 0,24 % cemento masės. Vandens atsiskyrimo koeficiento

sumažėjimas pasiekia atitinkamai 99 %, 100 %, 83 % vertes, DSANV kiekį padidinant iki 0,24 % cemento masės kartu su LS, NF ir PCE.



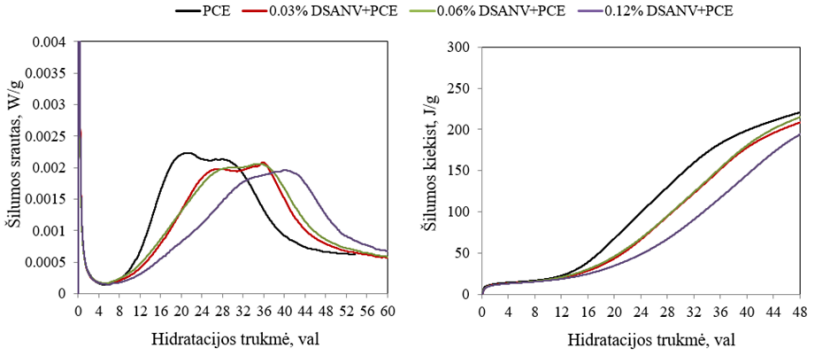
S3.4 pav. Cemento tešlos, modifikuotos daugiasluoksnių anglies nanovamzdelių suspensija ir plastifikuojančia įmaiša, vandens atsiskyrimas

Nanomodifikuotų cemento tešlų hidratacijos procesų tyrimams atlikta kalorimetrinė analizė su šilumos išsiskyrimo matavimais cemento hidratacijos proceso metu, siekiant išsiaiškinti DSANV įtaką hidratacijai su Pl ir be jų.

Iš cemento tešlos, modifikuotos DSANV suspensija (su CMC) šilumos srauto kalorimetrinės kreivės nustatyta, kad bandinių su DSANV suspensija indukcinis periodas yra ilgesnis nei etaloninio bandinio be DSANV. Šis laikotarpis pailgėja 36, 48 ir 72 min bandiniams, kuriuose DSANV kiekis atitinkamai 0,03, 0,06 ir 0,12 % cemento masės. Hidratacijos reakcijos greitėjimo periodas bandiniuose su DSANV priedu vyksta mažiau intensyviai ir reakcijos greičio piko aukštis mažesnis palyginus su etaloniniu bandiniu be DSANV. Bandinių su DSANV maksimalaus hidratacijos greičio pikas pasireiškia 1h vėliau esant 0,03, 0,06 % cemento masės ir 1 h 30 min vėliau esant 0,12 % cemento masės palyginus su etaloniniu bandniu be DSANV. Antrojo lėtėjimo periodo, kurį sukelia aliuminato hidratacijos reakcija ir galutinis ettringito susidarymas, petys išsiplečia didėjant DSANV kiekiui iki 0,12 % cemento masės.

Kompleksinė DSANV suspensijos su Pl įtaka cemento hidratacijai buvo išbandyta atliekant kalorimetrinį tyrimą su DSANV kiekiais nuo 0,03 % iki 0,12 % cemento masės ir Pl kiekiu lygiu 1% cemento masės. DSANV ir LS suspensijos modifikuoto cemento tešlos indukcinis periodas nesikeitė esant DSANV kiekiui 0,03 % ir 0,06 % cemento masės ir pailgėjo 1h, kai DSANV kiekis buvo 0,12% cemento masės, palyginus su etaloniniu bandiniu (cemento tešla, modifikuota tik LS). DSANV pridėjimas prie cementinio mišinio su LS sumažino hidratacinės šilumos piko aukštį ir pailgino šio piko atsiradimo laiką 14 h, kai DSANV kiekis padidėjo iki 0,12 % cemento masės. Aliuminato hidratacijos reakcijos ir ettringito susidarymą charakterizuojantis petys išsiplečia palyginus su etaloniniu mėginiu (modifikuotu tik LS), padidinus DSANV dozę iki 0,12 %.

DSANV taikymas cementiniuose mišiniuose su NF sukelia indukcinio hidratacijos periodo pailgėjimą 30 min, 30 min ir 1 h, kai DSANV kiekis yra atitinkamai 0,03, 0,06 ir 0,12 % cemento masės palyginus su etaloniniu bandiniu (cemento tešla su NF be DSANV suspensijos). Cemento tešlų su DSANV ir NF hidratacijos greičio kreivės pikas šiek tiek sumažėja (apie 5 %) palyginus su NF modifikuotu bandiniu be DSANV ir DSANV kiekio padidėjimas nuo 0,03 iki 0,12 % cemento masės lemia vėlesnį piko atsiradimą atitinkamai 2 h, 3 h ir 6 h palyginus su etalonine cemento tešla. Padidinus DSANV kiekį nuo 0 iki 0,12 % cemento masės kartu su NF, hidratacijos greitėjimo petys pailgėjo, o antruoju lėtėjimo periodu atsirado žymiai ryškesnė smailė palyginus su etaloniniu bandiniu, modifikuotu tik NF. Šie pokyčiai rodo aliuminato hidratacijos ir ettringito susidarymo procesų suintensyvėjimą.



S3.5 pav. Cemento tešlų, modifikuotų daugiasluoksnių anglies nanovamzdelių suspensija ir polikarboksilato eteriu , kalorimetrinės kreivės: a) šilumos srauto ir b) bendro šilumos kiekio

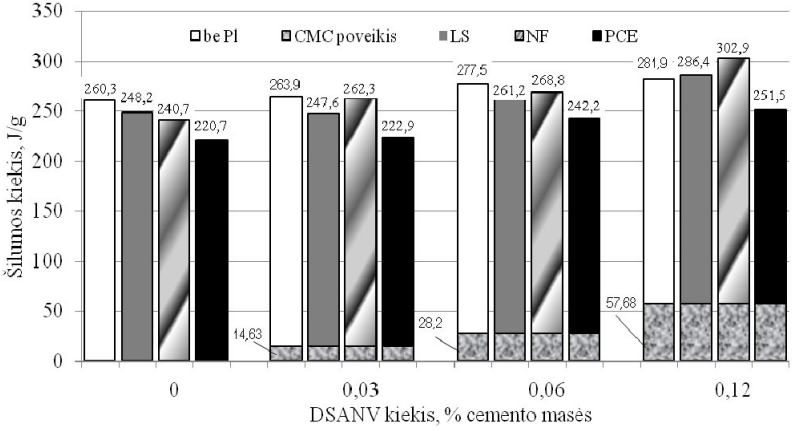
DSANV įvedimas nuo 0,03 iki 0,12 % cemento masės į cementimį mišinį su PCE neturi įtakos hidratacijos indukciniam periodui, kaip parodyta S3.5 paveiksle. Hidratacijos greičio didėjimo periodui būdingas didžiausio hidratacijos greičio piko sumažėjimas, kai cemento sistemos modifikavimui naudojamas DSANV kiekis nuo 0,03 % iki 0,12 % cemento masės su PCE. 0,12 % DSANV kiekis pailgina šio piko atsiradimą 14 h palyginus su etalonine cemento tešla (cemento tešla tik su PCE).

Padidinus DSANV kiekį nuo 0 iki 0,12 % padidėja šilumos išsiskyrimo petys antruoju lėtėjimo periodu. Šis poveikis nebuvo pastebėtas etaloniniame bandinyje tik su PCE. Antrojo lėtėjimo periodas prailgėjo. Pastebėtas poveikis susijęs su aliuminato hidratacijos reakcijos ir ettringito susidarymo pokyčiais, kuriuos sukelia DSANV suspensija.

Cemento tešlos, modifikuotos DSANV ir PCE, bendro šilumos kiekio kalorimetrinės kreivės pateiktos S3.5b paveiksle rodo šiluminės energijos kiekio sumažėjimą pridėjus DSANV nuo 0,03 iki 0,12 % cemento masės. Pridėjus DSANV iki 0,12 % cemento masės, bendras hidratacinės šilumos kiekis sumažėja nuo 220,7 J/g iki 193,8 J/g po 48 h cemento tešlos hidratacijos.

Norint nustatyti CMC įtaką cemento hidratacijos procesams buvo atliktas kalorimetrinis tyrimas cemento tešlai, modifikuotai CMC 0,04, 0,07 ir 0,14 %, kuris parodė,

kad esan tokiam CMC kiekiui hidratacinės šilumos sumažėjimas lygus atitinkamai 14,6 J/g, 28,2 J/g ir 57,7 J/g po 48 h hidratacijos.



S3.6 pav. Daugiasluoksnių anglies nanovamzdelių poveikis cemento hidratacinės šilumos kiekiui, išsiskyrusiam per 48 val.

Atsižvelgiant į CMC poveikį redukuoti hidrataciės šilumos kiekio pokyčiai didėjant DSANV iki 0,12 % cemento masės be plastifikuojančių įmaišų ir su jomis pateikti S3.6 paveiksle. Rezultatai rodo pastovų hidratacinės šilumos kiekio didėjimą didinant DSANV priedo kiekį.

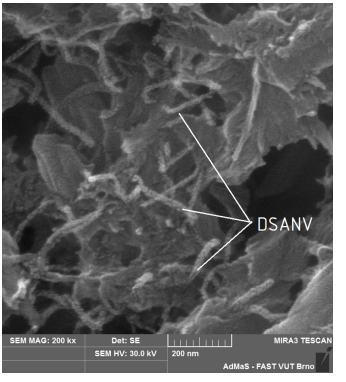
XRD buvo atliktas sukietėjusiai cemento tešlai, modifikuotai nuo 0, 03 iki 0, 12 % cemento masės po 28 parų kietėjimo. Etaloninės cemento tešlos (be DSANV) rentgenograma parodė portlandito $Ca(OH)_2$ susidarymą, kalcio karbonato $CaCO_3$ smailes ir kalcio hidrosilikato (C-S-H) amorfinius junginius. Cemento tešlos modifikavimas DSANV nuo 0,03 iki 0,12 % cemento masės nesukelia naujų fazių susidarymo cementiniame akmenyje po hidratacijos. Cemento bandinių su skirtingu DSANV kiekiu kiekybinė Rietveld fazinė analizė parodė skirtingą pagrindinių hidratacijos produktų kiekį po cemento hidratacijos (S3.1 lentelė). Iš S3.1 lentelės matyti, kad DSANV priedas nuo 0,03 % iki 0,12 % padidina nehidratuoto C_3S mineralo kiekį cementiniame akmenyje, kas rodo, kad sulėtina C_3S hidrataciją. Su tuo susijęs ir portlandito mineralo sumažėjimas modifikuotame cementiniame akmenyje. Tuo tarpu kubinės modifikacijos C_3A ir C_2S mineralų sumažėjimas cementiniame akmenyje rodo jų hidratacijos procesų pagreitėjimą ir aktyvų kalcio hidroaliuminatų formavimąsi cementiniame akmenyje. Nehidratuotos C_3S mineralo padidėjimas DSANV modifikuotame cementiniame akmenyje nuo 8,26 % iki 11,07 % gali būti susijęs su hidratacijos procesų intensyvumo sumažėjimu dėl CMC įtakos, kuris koreliuoja su aukščiau pateiktais hidratacijos kinetikos rezultatais. Nanomodifikuoto cementinio akmens amorfininių junginių kiekis, DSANV kiekiui padidėjus iki 0,12 % cemento masės, padidėja nuo 48,43 % iki 50,31 %. Amorfinių junginių kiekio padidėjimą gali sukelti padidėjęs submikrokristalų (amorfinių junginių) kiekis, susidarantis hidratuojant kalcio silikatų ir kalcio aliuminato mineralams.

Remiantis DSANV modifikuoto cementinio akmens TG/DTG analize, buvo nustatyti endoterminiai efektai 100–200 °C, 430–450 °C ir 650–700 °C temperatūroje. Smailė 100–200 °C temperatūros diapazone charakterizuoja cemento hidratacijos produktų, tokių kaip kalcio hidrosilikatai, kalcio hidroaliuminatai ir ettringitas, dehidrataciją. Antroji smailė 430–450 °C temperatūroje atitinka portlandito skilimą. Paskutinė smailė 650–700 °C temperatūroje yra susijusi su kalcito skilimu. DSANV pridėjimas nesukėlė naujų smailių termogramose esant skirtingiems DSANV kiekiams. Cemento tešlų, modifikuotų DSANV nuo 0 iki 0,12 % cemento masės ir kietintų 28 paras normaliomis sąlygomis, TG/DTG analizės rezultatai nerodo jokių skirtumų, t. y. neatsiranda naujų cemento hidratacijos produktų.

S3.1 lentelė. Nanomodifikuoto cementinio akmens kiekybinė analizė Rietveld fazinės analizės metodu

Junginys	0 % DSANV	0,03 % DSANV	0,06 % DSANV	0,12 % DSANV
C_3S monoklininis (NISHI)	8,26	9,11	10,70	11,07
C_2S beta (MUMME)	8,85	8,34	8,13	7,33
C_3A kubinis	1,38	1,09	0,70	0,69
C_4AF	2,05	2,62	1,41	2,27
Amorfinė fazė	48,43	47,10	50,70	50,31
Portlanditas, sintetinis	19,72	18,70	16,32	16,32

Siekiant nustatyti DSANV poveikį cemento hidratacijos produktų morfologijai buvo atliktas cementinio akmens mikroskopinė analizė, naudojant SEM. Paruošta cemento tešla, kurios V/C santykis lygus 0,5, buvo kietinta vandenyje (20±1,0) °C temperatūroje 3 paras. SEM analizė buvo atlikta stebint skeltą sukietėjusio cementinio akmens paviršių. SEM tyrimų metu gautas DSANV modifikuoto cementinio akmens vaizdas pateiktas S3.7 paveiksle.



S3.7 pav. Daugiasluoksnių anglies nanovamzdelių vaizdas sukietėjusiame cementiniame akmenyje

DSANV chemiškai nereaguoja su cemento hidratacijos produktais, ką patvirtina grynas jų paviršius, be hidratacijos produktų užuomazgų nanovamzdelių paviršiuje. Didelis DSANV santykis tarp ilgio ir skersmens paaiškina jų gebėjimą lankstytis tarp cemento hidratacijos produktų paviršiaus ir formuoti ryšulius porų tūryje. Cemento hidratacijos produktų kristalų formavimasis prasideda DSANVpaviršiuje arba aplink jį. Šį procesą inicijuoja DSANV tolygiai pasiskirstę vandenyje cemento hidratacijos proceso metu.

SEM atskleidė DSANV tolygų pasiskirstymą cemento hidratacijos produktuose ir cheminės sąveikos tarp jų nebuvimą. DSANV poveikis cemento hidratacijos produktų morfologijai vyksta per kristalizacijos iniciavimo, armavimo ir užpildymo efektus. Tačiau, norint prognozuoti cementinių medžiagų savybes skystoje ir sukietėjusioje būsenoje, reikia atsižvelgti į DSANV gebėjimą aglomeruotis ir formuoti ryšulius dėl jų didelio ilgio ir skersmens santykio ir mažo sukibimo su cemento hidratacijos produktais.

Nano modifikuotų cemento tešlų po 7 parų kietėjimo išdžiovintų 60 °C teperatūroje azoto adsorbcijos ir desorbcijos porometrija (NADP) parodė, kad DSANV kiekis nuo 0 iki 0,12 % cemento masės neturi įtakos suminiam cementinio akmens porų tūriui. Suminis porų tūris pakinta nuo 0,064 cc/g iki 0,060 cc/g. Nanomodifikuotų bandinių su skirtingu DSANV kiekiu mikroporingumo parametrai pateikti S3.2 lentelėje.

S3.2 lentelė. Mikroporingumo parametrai

Bandinio žymuo	0 % DSANV	0,03 % DSANV	0,06 % DSANV	0,12 % DSANV
Suminis porų tūris, cc/g	0,064	0,062	0,060	0,060
Porų paviršiaus plotas, m^2/g	15,363	12,947	13,495	11,670

DSANV modifikuotų cemento tešlų porų paviršiaus plotas sumažėja nuo 15,363 m^2/g (etaloniniam bandiniui beDSANV) iki 11,670 m^2/g, esant DSANV kiekiui 0,12 % cemento masės. Šie rezultatai siejami su nanomodifikuotų cemento sistemų hidratacijos procesų pokyčiais ir cemento hidratacijos produktų morfologijos pokyčiais, kurie pastebėti anksčiau aprašytuose XRD, FTIR ir SEM tyrimuose.

Bendrosios išvados

1. Optimalus DSANV suspensijos homogenizavimo metodas – 6 min trukmės 400 W intensyvumo ir 20 kHz dažnio ultragarsinis poveikis leidžia išlaikyti DSANV suspensiją tinkamo homogeniškumo vieną mėnesį.
2. Mišinių tiksotropiškumo/dilatantiškumo reologinę elgseną nulemia naudojamos plastifikuojančios įmaišos tipas, nuo DSANV kiekio ji nepriklauso cemento tešlose be plastifikuojančios įmaišos ir su LS bei NF plastikliais. Komplekse su PCE plastikliu DSANV sumažina cemento tešlos dilatantiškumą.
3. DSANV su ir be plastifikuojančių įmaišų didina cementinių mišinių ribinius šlyties įtempius ir plastinį klampį. Cementiniuose mišiniuose, modifikuotuose DSANV iki 0,24 % cemento masės be plastifikuojančių įmaišų ir naudojant LS ir NF plastifikuojančias įmaišas, ribinių šlyties įtemių ir plastinio klampio

padidėjimas neviršija 20 % ir toks modifikavimas neturi didelės įtakos šių įmaišų plastifikavimo efektyvumui. Kompleksinis cemento tešlos modifikavimas DSANV ir PCE plastifikuojančia įmaiša padidina ribinius šlyties įtempius ir plastinį klampį ir sumažina šios įmaišos plastifikavimo efektyvumą DSANV kiekiui atitinkamai viršijus 0,03 % ir 0,015 % cemento masės. Cemento tešlos, modifikuotos DSANV su PCE plastifikuojančiua įmaiša ribiniai šlyties įtempiai ir plastinis klampis padidėja 265 % ir 107 % esant DSANV kiekiui 0,12 % cemento masės dėl DSANV kartu su CMC sąveikos su PCE funkcinėmis grupėmis. Šią sąveiką patvirtina FTIR spektroskopija, kuri rodo vandenilinių jungčių virpesių smailės intensyvumo padidėjimą 3200–3600 cm^{-1} diapazone.

4. Cemento tešlų, modifikuotų DSANV be plastifikuojančios įmaišos ir su LS bei NF plastifikuojančiomis įmaišomis ribiniai šlyties įtempiai ir plastinis klampis padidėja (iki 23 %) per 120 min po cemento tešlos sumaišymo. Cemento tešlų, modifikuotų DSANV su PCE plastifiuojančia įmaiša, ribiniai šlyties įtempiai ir plastinis klampis nežymiai sumažėja (iki 11 %) per 120 min po cemento tešlos sumaišymo esant DSANV kiekiui didesniam negu 0,03 % cemento masės.
5. Cemento tešlos modifikavimas DSANV padidina cementinių mišinių stabilumą, atitinkamai sumažindamas vandens atsiskyrimo koeficientą 85 %, 99 %, 100 % ir 83 % padidinus DSANV be plastifikuojančių įiemaišų ir su LS, NF ir PCE plastifikuojančiomis įmaišomis kiekį iki 0,24 % cemento masės.
6. Įvertinus DSANV suspensijoje esančios CMC įtaką, DSANV be ir su plastifikuojančiomis įmaišomis nežymiai pagreitina cemento hidratacijos procesus ir padidina hidratacinės šilumos išsiskyrimą. 0,12 % DSANVpriedas be ir su plastifikuojančiomis įmaišomis LS, NF ir PCE padidina išsiskiriančios hidratacinės šilumos kiekį 21,6, 38,2, 62,2 ir 30,8 J/g po 48 h hidratacijos.
7. DSANV modifikuotos cemento tešlos rentgeno difrakcinė, kombinuota terminė analizė ir FTIR spektroskopija nenustatė naujų junginių cemento hidratacijos produktuose. Remiantis kiekybine Rietveldo mineralinės sudėties analize galima teikti, kad cementinių medžiagų modifikavimas DSANV pagreitina C_3A ir C_2S ir sulėtina C_3S cemento mineralų hidratacijos procesus portlandcemenčio hidratacijos metu.
8. DSANV keičia cemento hidratacijos produktų morfologiją. DSANV chemiškai nereaguoja su cemento hidratacijos produktais, ką patvirtina grynas jų paviršius, jos išsidėsto šalia cemento hidratacijos produktų paviršiaus ir gali formuoti ryšulius porų tūryje. DSANV kiekio padidinimas nuo 0 iki 0,12 % cemento masės neturi įtakos suminiam cemento tešlos porų tūriui ir sumažina porų paviršiaus plotą 24 % dėl porų stambumo padidėjimo, kas gali būti siejama su cemento hidratacijos procesų ir hidratacijos produktų morfologijos pokyčiais.

Annexes[1]

Annex A. Flow Curves of Cement Pastes Modified by Multi-walled Carbon Nanotubes Suspension with and without Plasticizing Admixtures

Annex B. Approximation Equations for Cement Pastes Modified by Multi-Walled Carbon Nanotubes Suspension with and without Plasticizing Admixtures according to Herschel-Bulkley Rheological Model

Annex C. Quantitative Rietveld Phase Analysis

Annex D. Simultaneous Thermal Analysis

Annex E. Declaration of Academic Integrity

Annex F. The Coauthors' Agreements to Present Publications Material in the Dissertation

Annex G. Copies of Scientific Publications by the Author on the Topic of the Dissertation

[1]The annexes are supplied in the enclosed compact disc.

Ekaterina KARPOVA

INFLUENCE OF CARBON NANOTUBES ON
THE EFFECTIVENESS OF PLASTICIZERS,
HYDRATION AND STRUCTURE OF
CEMENT-BASED MATERIALS

Doctoral Dissertation

Technological Sciences,
Material Engineering (T 008)

ANGLIES NANOVAMZDELIŲ POVEIKIS
PLASTIFIKUOJANČIŲ ĮMAIŠŲ EFEKTYVUMUI,
CEMENTINIŲ MIŠINIŲ
HIDRATACIJAI IR STRUKTŪRAI

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